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TOUGHNESS OF BITUMINOUS AGGREGATES

By CHARLES S. REEVE, *Chemist*, and RICHARD H. LEWIS, *Assistant Chemist, Office of Public Roads and Rural Engineering, United States Department of Agriculture*

INTRODUCTION

The following investigation was instituted as a result of certain observations on the part of one of the authors through an extended inspection of a large mileage of bituminous-concrete roads in New England. The mixes were largely of the one-size stone type, using crusher run of approximately the size that would pass a 1¼-inch screen and be retained on a ½-inch screen. The predominating rocks used were field stone of granitic or gneissoid character. The exceptions were a few sections constructed with quartzite or trap rock. Coal-tar binders were used almost exclusively in this work, and in most cases they were fluid products of about the consistency commonly required for hot-surface applications.

The careful inspection of a large mileage of roads constructed by the mixing method with the materials above noted showed conclusively a more pronounced and frequently quite rapid failure of sections in which trap rock or quartzite was used than in those sections constructed with native field stone. In fact, the difference in behavior was so marked that one engineer ventured the observation that trap rock was not adapted to bituminous construction. The excellent behavior of the tar trap-rock sections constructed by the same method and exposed to heavy traffic at Jamaica, N. Y.,[1] offered positive evidence to the contrary, although it is to be noted that a heavier grade of tar product was used than had been the case in the New England work. There appeared, however, to be no room for doubt that various rocks behaved differently in combination with the same bitumen, and it was in an endeavor to determine, if possible, what particular characteristic was responsible for the difference in behavior that the experimental work described in this paper was undertaken.

EXPERIMENTAL DATA

A number of large representative samples of various types of rock were selected, including those which had been under observation in the construction above referred to. The samples were passed through a small jaw crusher and reduced to particles ranging in size from ¼ inch

[1] PROGRESS REPORTS OF EXPERIMENTS IN DUST PREVENTION AND ROAD PRESERVATION, 1911. U. S. Dept. Agr. Off. Pub. Roads Circ. 98, 47 p. 1912.

in diameter to dust. The particles were separated into definite sizes by screening and were then recombined in fixed proportions with the object of producing an aggregate that, on a small scale, fairly well represented the one-size stone aggregate. The accurately proportioned aggregate was heated and mixed with a predetermined proportion of bituminous material. In order that the relative amount of bitumen to aggregate would be the same in all mixtures, the precentage was figured as a rational proportion, taking into account the specific gravity of both the rock and bitumen in accordance with the suggestion of Hubbard.[1] The aggregate and bitumen were heated separately to 150° C. and then thoroughly mixed together, after which the mix was allowed to cool to 105° and maintained at that temperature in a 105° oven until the test specimens were molded. The specimens were 25 by 25 mm. cylinders, compressed with a die and plunger under a pressure of 132 kgm. per square centimeter on the machine commonly used for preparing specimens in rock testing to show their cementing values.[2] At the end of 24 hours and of 7 days the cylinders were tested for toughness on the Page impact machine[2] with a 500-gm. hammer. The specimens were stored under cover in the laboratory until half an hour before testing, and during the 7-day period were immersed in water at 25° in order to bring them to a uniform temperature for testing. An average was taken of the results on three cylinders, and it may be stated that in all cases the three cylinders gave results in very close agreement.

Rocks of which the physical tests are given in Table I were used in the first series of experiments. After crushing, the particles were recombined in the following proportion:

Passing 8-mesh, retained on 10-mesh sieve..... 25 per cent.
Passing 10-mesh, retained on 20-mesh sieve..... 25 per cent.
Passing 20-mesh, retained on 50-mesh sieve..... 50 per cent.

TABLE I.—*Physical tests of rock used in preliminary toughness work*

No.	Rock.	Locality.	Specific gravity.	Weight per cubic foot.	Wear.	French coefficient.	Hardness.	Toughness.	Cementing value.	Absorption.
				Lbs.	*P.ct.*					
6112	Biotite gneiss	Fairfield, Conn.	2.62	163	3.0	13.3	18.0	11	16	1.02
5589	Quartzite	Providence, R. I.	2.61	162	4.4	9.0	19.3	16	5	.47
1817	Metamorphic sandstone	Newport, R. I.	2.72	170	4.8	8.3	18.3	16	17	.59
7316	Diabase	Montgomery County, Md.	2.92	182	1.9	20.6	19.2	28	102	.45
7682	Biotite gneiss	Delaware County, Pa.	2.79	174	2.8	14.3	18.6	13	14	.20
7445	Sandstone	Picture Rocks, Pa.	2.66	166	2.6	15.5	19.2	19	43	1.72
4813	Open-hearth slag	Cape Breton, Canada	3.29	205	3.1	12.9	.....	.....	500+	1.68
7332	Limestone	Jack County, Tex.	2.66	166	3.8	10.6	14.1	6	118	1.27
6710	Blast-furnace slag	Canal Dover, Ohio	2.81	175	2.4	16.5	11.4	5	300	.....
4444	Basalt	Cowlitz County, Wash.	2.75	171	2.5	16.1	18.5	14	7	1.77
1820	Chlorite gneiss	Providence, R. I.	2.78	173	4.6	8.6	15.7	8	17	.46
871	.....do	Louisa County, Va.	3.55	221	8.1	4.9	.....	3	.....	.16

[1] HUBBARD, PRÉVOST. THE BITUMEN CONTENT OF COARSE BITUMINOUS AGGREGATES. *In* Proc. Intern. Assoc. Testing Materials, v. 2, no. 11, art. 25, pt. 2, 7 p. 1912.

[2] JACKSON, F. H., Jr. METHODS FOR THE DETERMINATION OF THE PHYSICAL PROPERTIES OF ROAD-BUILDING ROCK. U. S. Dept. Agr. Bul. 347, 27 p., 12 fig. 1916.

Two grades of refined water-gas tar, X and Y, were used. The latter was of the consistency used frequently in bituminous-concrete construction, and that there might be no question about the similar character of the two tars, X was prepared by adding a proper amount of heavy water-gas-tar distillate to Y, producing a tar of the consistency used commonly in hot surface treatment, and also in bituminous concrete in some New England localities, as noted above. In addition to these two tars, a residual petroleum, No. 6408, an oil asphalt, No. 6409, and a fluxed native asphalt, No. 5767, were used. The characteristics of all the bituminous materials are given in Tables II and III.

TABLE II.—*Analyses of water-gas tar*

Sample No.	X	Y	X′	Y′
Specific gravity (25°/25° C.)	1. 168	1. 184	1. 162	1. 184
Float test (32° C.)	1′ 48″	.....	1′ 44″	.....
Float test (50° C.)	49″	2′ 21″	.....	2′ 50″
Bitumen soluble in carbon bisulphid, per cent.	99. 23	99. 25	99. 23	99. 23
Organic matter insoluble (free carbon), per cent.	0. 72	0. 70	0. 75	0. 72
Inorganic matter insoluble.....per cent.	0. 05	0. 05	0. 02	0. 05
Distillate (270°–315° C.) by weight, per cent.	.....	.....	13. 4	2. 48
Pitch (over 315° C.) by weight...per cent.	.....	.....	86. 6	97. 43

TABLE III.—*Analyses of petroleum and asphalt products*

Sample No.	6408	6409	5767	8950	8949	8948	8748
	A	B	C	D	E	F	G
Material	Residual petroleum.	Oil asphalt.	Fluxed native asphalt.	Oil asphalt.	Oil asphalt.	Oil asphalt.	Fluxed native asphalt.
Specific gravity (25°/25° C.)	0. 988	1. 010	1. 044	1. 036	1. 046	1. 048	1. 050
Specific viscosity (Engler 100° C.)	47	.....	.....	.....	.....	.....	.....
Float test (32° C.)	7′ 20″	.....	.....	.....	.....	.....	.....
Float test (50° C.)	1′ 45″	.....	.....	.....	.....	.....	.....
Melting point (° C.)	.....	54	52. 5	45. 7	51. 8	62. 4	44
Penetration (100 gm., 5 sec., 25° C.)	.....	111	122	145	91	50	118
Loss (163° C., 5 hours)	1. 17	0. 62	3. 08	0. 46	0. 16	0. 09	1. 16
Float test of residue (50° C.)	2′ 38″	.....	.....	.....	.....	.....	.....
Penetration of residue (25° C.)	.....	78	65	87	55	37	65
Bitumen soluble in carbon bisulphid.....per cent.	99. 96	99. 96	95. 54	99. 95	99. 92	99. 84	95. 69
Organic matter insoluble, per cent.	0. 04	0. 04	1. 84	0. 05	0. 06	0. 10	1. 12
Inorganic matter insoluble, per cent.	0	0	1. 62	0	0. 02	0. 06	3. 19
Total bitumen insoluble in 86° B. naphtha..per cent.	21. 35	28. 14	22. 29	25. 65	29. 47	29. 76	24. 32
Fixed carbon.....per cent.	11. 08	13. 65	10. 62	15. 26	17. 60	18. 05	12. 52

A rational volume proportion of 88 per cent of aggregate to 12 per cent of bitumen was adopted, and the weight proportions for each combination of materials was figured on the basis of this volume ratio.

All the cylinders in the first series of tests were broken at the end of 24 hours, and the results are given in Table IV. Where zero toughness is indicated, the cylinder was deformed by the mere weight of the plunger's resting upon it. The results in Table IV are tabulated in the order of the increasing strength of the cylinders containing the lightest water-gas tar, and, for convenience, the physical tests of the rocks in Table I are given in the same order. The difference in the relative binding value of the different mixtures is clearly apparent, and it also is definitely shown that certain rocks yield a relatively tough mixture in combination with what generally would be considered a rather fluid tar for bituminous construction. However, it will be noted that there is no single physical property which appears to be responsible for this difference in behavior when the rocks are combined with a bituminous material.

TABLE IV.—*Toughness tests on bituminous-aggregate cylinders*

No.	Rock.	Toughness.				
		Refined water-gas tar.	Refined water-gas tar.	Residual petroleum.	Oil asphalt.	Fluxed. native asphalt
		X	Y	A	B	C
6112	Biotite gneiss	0	7	1	4	10
5589	Quartzite	0	10	2	5	12
1817	Metamorphic sandstone	0	13	3	6	12
7316	Diabase	0	14	2	5	13
7682	Biotite gneiss	3	9	2	5	9
7445	Sandstone	4	12	4	5	13
4813	Open-hearth slag	6	14	0	5	10
7332	Limestone	6	17	8	8	14
6710	Blast-furnace slag	7	11	3	4	10
4444	Basalt	7	12	5	6	11
1820	Chlorite gneiss	8	15	6	9	14
871	.....do	10	17	4	8	15

Upon the disclosure of these interesting differences, for which no explanation was apparent, a second series of tests was decided upon in which several possible sources of error could be avoided. The crushed material, for instance, was obtained directly from the block out of which had been cut the sections for specific gravity and absorption and the core pieces for hardness and toughness, whereas in the first series the crushed rock was taken from that remaining in a sack after the regular laboratory tests had been made. This change in method tied up the physical tests directly with the material used in preparing the bituminous aggregates. In order to reduce to some extent the possibility of errors due to varia-

tions in the relative proportions of different size particles in one of the fractions of crushed aggregate used, a 30-mesh screen was introduced in separating the aggregate. The mineral aggregate for the second series of cylinders was therefore proportioned as follows:

Passing 8-mesh, retained on 10-mesh screen..... 25 per cent.
Passing 10-mesh, retained on 20-mesh screen..... 25 per cent.
Passing 30-mesh, retained on 50-mesh screen..... 50 per cent.

It is likely that this elimination of an intermediate size of particle is partly responsible for the uniformly lower results obtained throughout the second series. The physical tests on the rocks used are given in Table V. The bituminous materials consisted of refined water-gas tars practically identical with those used in the first series, three oil asphalts of 145, 91, and 50 penetration, respectively, and a fluxed native asphalt. The data regarding these materials will be found in Tables II and III.

TABLE V.—*Physical tests of rocks used in second series of toughness tests*

Lab. No.	Rock.	Locality.	Specific gravity.	Weight per cubic foot.	Wear.	French coefficient.	Hardness.	Toughness.	Cementing value.	Absorption.
				Lbs.	*P. ct.*					
10101	Diabase	Montgomery County, Md.	3.05	190	1.4	28.6	18.5	21	.....	0.35
9093	Biotite schist	Cumberland, Me.	2.75	171	6.1	6.6	18.0	8	35	.41
10108	Quartzite	Minnehaha, S. Dak.	2.67	167	2.8	14.3	19.3	17	5	.68
9445	Biotite granite	Knox County, Me.	2.64	165	3.1	12.9	19.7	17	12	.40
9095	Biotite gneiss	Cumberland County, Me.	2.74	171	4.8	8.3	18.8	8	30	.26
9094	Altered diabase porphyry.	Cumberland, Me.	2.94	184	2.3	17.4	18.3	18	44	.27
8136	Feldspathic sandstone	Montgomery County, Md.	2.46	153	4.8	8.3	15.5	5	111	3.15
8992	Open-hearth slag	Mahoning County, Ohio.	3.60	228	4.7	8.5	.....	....	84	.12
9321	Feldspathic quartzite	Fulton County, Ga.	2.63	163	5.1	7.8	18.5	20	8	.33
8993	Blast-furnace slag	Mahoning County, Ohio.	2.89	180	7.7	5.2	18.0	14	96	1.18
8989	Chlorite gneiss	Jamestown, R. I.	2.70	168	6.2	6.5	18.0	14	20	.21
9281	Limestone	Seneca County, Ohio.	2.66	166	4.3	9.3	13.5	7	20	2.16

Before deciding upon the proportions of bitumen to be used in this series of tests, a number of cylinders were made up with concrete sand which had been screened and reproportioned in the same manner as adopted for the rock-test pieces. The oil asphalt 8950 was used, and the results in three cylinders for each proportion are given in Table VI. Since the proportion of 88 aggregate to 12 bitumen, which was used in the first series of tests, gave within one point of the highest toughness obtained, it was decided to continue its use through the second series. This series of results with the sand and bitumen mixtures shows very clearly within what narrow limits the percentage of bitumen should be controlled in order to obtain its maximum efficiency as a binder. By taking the highest toughness obtained, which is 11, it will be seen that this was produced within a range of bitumen content of 0.43 per cent by weight and that well-defined decreases continue from this maximum by either reducing or increasing the bitumen content.

TABLE VI.—*Effect on toughness of variation of rational proportion of bitumen and sand*

Test No.	Rational proportion.		Percentage of bitumen by weight.	Toughness.
	Rock.	Bitumen.		
1	93	7	2.86	3-3-3
2	92	8	3.29	4-4-4
3	91	9	3.72	6-6-6
4	90	10	4.15	7-7-7
5	89	11	4.58	8-8-8
6	88	12	5.01	10-10-10
7	87	13	5.44	11-11-11
8	86	14	5.87	11-10-11
9	85	15	6.30	10-10-10
10	84	16	6.73	9-9-9
11	83	17	7.16	8-8-8
12	82	18	7.59	6-6-6
13	81	19	8.02	5-5-5

For the more complete information of the reader Table VII gives the percentage by weight of each bituminous material used with each rock. In this and all other tables the rocks are arranged in the order of increasing toughness with the light refined water-gas tar at the end of 24 hours. The results obtained in this series are given in Table VIII. While, as above noted, they are uniformly lower than those obtained in the first series, it will be seen that the various rocks bear the same general relation to each other, as shown in Table IV, for the first series of tests. With the light water-gas tar X′, for instance, the diabase and quartzite continue to exhibit no strength whatever, while the chlorite gneiss shows up well from a strength standpoint. This bears out fully the observations made in the actual construction work which led to this investigation, where the bulk of the work referred to was constructed with these three types of rock, and the chlorite gneiss was the only one which showed any pronounced success in combination with the relatively fluid tar binders. It also may be noted with interest that the feldspathic sandstone 8136 shows a marked weakness in combination with all the binders, which is clearly shown in the right-hand column of averages of all results obtained on each type of rock. This accords with some results obtained recently in actual practice on experimental sections constructed by this office. The same rock from which a sample was taken for these tests was used in a one-size stone bituminous concrete with both oil asphalt and fluxed native asphalt of 102 and 117 penetration, respectively. The section began to check and crack almost immediately, and in a few months began to fail so generally that a surface treatment was necessary in order to save it.

TABLE VII.—*Percentages of weight of bitumens used in mixtures on basis of rational proportion of 88 parts of mineral aggregate to 12 parts of bitumen*

Sample No.	Name of rock.	Specific gravity of rock.	Percentage by weight.					
			Refined water-gas tar.		Oil asphalt.	Oil asphalt.	Oil asphalt.	Fluxed native asphalt.
			X′	Y′	8950	8949	8948	8748
	Sand	2.65	5.65	5.75	5.06	5.10	5.12	5.13
10101	Diabase	3.05	4.93	5.03	4.42	4.46	4.47	4.48
9093	Biotite schist	2.78	5.39	5.49	4.83	4.90	4.91	4.92
10108	Quartzite	2.67	5.60	5.70	5.05	5.06	5.08	5.09
9445	Biotite granite	2.65	5.65	5.75	5.06	5.10	5.12	5.13
9095	Biotite gneiss	2.73	5.48	5.58	4.92	4.96	4.98	4.99
9094	Altered diabase porphyry	2.94	5.11	5.20	4.58	4.62	4.63	4.64
8136	Sandstone	2.54	5.87	5.97	5.27	5.31	5.32	5.34
8992	Open-hearth slag	3.55	4.27	4.36	3.82	3.86	3.88	3.89
9321	Feldspathic quartzite	2.67	5.60	5.70	5.05	5.06	5.08	5.09
8993	Blast-furnace slag	2.93	5.13	5.22	4.60	4.64	4.66	4.67
8989	Chlorite gneiss	2.75	5.45	5.55	4.88	4.93	4.94	4.95
9281	Limestone	2.72	5.50	5.60	4.94	4.98	5.00	5.02

TABLE VIII.—*Toughness tests on bituminous aggregate cylinders (second series)*

No.	Rock.	Toughness.												Average.
		24 hours.						7 days.						
		Refined water-gas tar.		Oil asphalt.			Fluxed native asphalt.	Refined water-gas tar.		Oil asphalt.			Fluxed native asphalt.	
		X′	Y′	D	E	F	G	X′	Y′	D	E	F	G	
	Sand	0	7	10	8	7	12	0	6	9	7	7	10	6.92
10101	Diabase	0	8	9	7	7	10	0	9	9	9	9	10	7.25
9093	Biotite schist	0	10	9	7	7	10	0	11	8	9	8	11	7.50
10108	Quartzite	0	10	9	9	8	8	0	11	12	11	8	10	8.00
9445	Biotite granite	0	11	10	8	8	11	0	11	9	7	8	11	7.83
9095	Biotite gneiss	0	6	9	10	8	11	1	9	9	8	9	12	7.67
9094	Altered diabase porphyry	0	11	9	9	9	11	5	12	10	10	7	12	8.75
8136	Feldspathic sandstone	1	7	8	5	5	6	4	6	6	5	5	7	5.42
8992	Open-hearth slag	2	11	8	9	7	10	2	12	11	11	8	10	8.42
9321	Feldspathic quartzite	2	13	10	9	10	12	3	15	9	9	9	12	9.42
8993	Blast-furnace slag	2	9	8	8	7	8	4	10	8	8	7	12	7.58
8989	Chlorite gneiss	3	11	7	9	8	10	4	11	8	8	7	11	8.08
9281	Limestone	6	11	10	8	7	10	9	14	10	8	8	13	9.50
	Average	1.23	9.62	8.92	8.15	7.54	9.92	2.46	10.54	9.08	8.46	7.70	10.85	....

In direct reference to these service results a review of some of the data developed in the two series of tests discloses some important relations. It will be noted, for instance, that the limestone, blast-furnace slag, and two chlorite gneisses show the lowest toughness of any of the rocks used in the first series. In combination with certain bituminous binders,

however, they yield toughness results which exceed, in some cases, those obtained with the solid rock itself. The limestone, with a toughness of 6, in only one case shows as low a toughness as this with a binder, and in combination with the refined water-gas tar Y develops a toughness of 17. The chlorite gneiss (871), which has a toughness of 3, in no case has as low a toughness as this when combined with any of the bituminous binders which were used; and in combination with the refined water-gas tar Y and the fluxed native asphalt, it yields toughness results as high as 17 and 15, respectively. A reference to Tables V and VIII shows the same behavior with most of the binders for the biotite schist, biotite gneiss, and, more noticeably, for the limestone. In comparing these tables it will be noted that all the binders fail to produce a relatively high toughness with the feldspathic sandstone, whose service results were referred to above. From these results it would appear that some modification of the toughness limits for bituminous macadam suggested by Hubbard and Jackson [1] could well be made to admit rocks of lower toughness than they would otherwise admit, provided such rocks can be made to develop a mixture of sufficient toughness through the introduction of a bituminous binder. In addition to cases heretofore cited where this has been done successfully the utilization of the coralline rocks or soft limestone of Florida offers an excellent example of the possibilities of such a practice. The majority of these rocks are so soft that a toughness cylinder can not be cut from them, but they have been used in bituminous macadam to form a tough and durable wearing surface when combined with a properly selected bituminous binder.

As a matter of interest the results obtained with each bituminous material have also been averaged in Table VIII, showing that the fluxed native asphalt gives the highest average result, with the heavy refined tar, Y′, a close second. A reference to these averages also shows that for the proportion of bitumen used in these tests the strength of the oil-asphalt specimens decreases with increase in hardness of the binder. It will be noted, however, that, as in the first series of tests, there is no apparent direct relation between any one physical characteristic of the rock and its behavior with a bituminous binder.

With the object of learning whether any single component of the rocks was responsible for this difference or behavior, the mineral composition of each was tabulated in the same order used in the other tables. The analyses, made in accordance with the method used in the laboratory of the Office of Public Roads and Rural Engineering,[2] are given in Table IX. From these results there does not appear to be any definite relation between the mineral composition and the toughness.

[1] HUBBARD, PRÉVOST, and JACKSON, P. H., jr. THE RESULTS OF PHYSICAL TESTS OF ROAD-BUILDING ROCK. U. S. Dept. Agr. Bul. 370, p. 11. 1916.

[2] LORD, E. C. E. RELATION OF MINERAL COMPOSITION AND ROCK STRUCTURE TO THE PHYSICAL PROPERTIES OF ROAD MATERIALS. U. S. Dept. Agr. Bul. 348, 26 p., 3 fig., 8 pl. 1916.

TABLE IX.—*Petrographic analyses of crystalline rocks used in toughness cylinders (second series)*

Rock.	Diabase (10101).	Biotite schist (9093).	Quartzite (10108).	Biotite granite (9445).	Biotite gneiss (9095).	Altered diabase porphyry (9094).	Feldspathic sandstone (8136).	Open-hearth slag (8992).	Feldspathic quartzite (9321).	Blast-furnace slag (8993).[a]	Chlorite gneiss (8989).
Augite	43.8	.....	.....	.....	.....	52.2	.....	.....	.....	.....	.....
Plagioclase	43.2	16.2	.....	16.4	.....	36.3	4.7	.....	.....	.....	.....
Orthoclase	.....	27.2	.....	38.8	26.6	.....	49.3	.....	63.8	.....	.....
Quartz	.....	31.4	94.2	32.1	54.0	.....	26.1	.....	28.8	.....	38.4
Biotite	.6	18.6	.....	6.4	16.8	.....	.....	.....	2.4	.....	2.8
Muscovite	.....	1.0	.....	.....	2.6	.....	1.0	.....	3.0	.....	.....
Limonite	.....	.....	.....	.....	.....	.....	18.7	.....	.....	.....	.....
Chlorite	5.6	.....	.....	.....	.....	.....	.2	.....	.....	.....	48.2
Epidote	.....	.....	.....	.....	.....	.....	.....	.....	.8	.....	3.9
Kaolin	3.4	3.6	2.6	5.8	.....	.....	.....	.....	.....	.....	.....
Hematite	.....	.....	3.2	.....	.....	.....	.....	.....	.....	.....	.....
Magnetite	3.4	1.0	.....	.5	.....	5.9	.....	.....	.....	.....	2.6
Garnet	.....	.....	.....	.....	.....	.....	.....	.....	1.0	.....	4.1
Apatite	.....	.4	.....	.....	.....	.....	.....	.....	.....	.....	.....
Titanite	.....	.6	.....	.....	.....	.....	.....	.....	.....	.....	.....
Pyrite	.....	.....	.....	.....	.....	.....	.....	.....	1.2	.....	.....
Calcite	.....	.....	.....	.....	.....	.2	.....	.....	.....	.....	.....
Serpentine	.....	.....	.....	.....	.....	5.4	.....	.....	.....	.....	.....
Belite	.....	.....	.....	.....	.....	.....	.....	49.8	.....	.....	.....
Iron ferrite	.....	.....	.....	.....	.....	.....	.....	47.2	.....	.....	.....
Iron	.....	.....	.....	.....	.....	.....	.....	3.0	.....	.....	.....

[a] Not analyzed.

On realizing that changes in the size of particles in the aggregate might have resulted from the effects of compressing the cylinders, the bitumen was extracted from the aggregates after the tests had been made, and the rock particles were graded again by sieve analysis. The results so obtained are given in Table X. Interesting changes were noted in the proportioning of the aggregate and, whereas none of the cylinders originally contained any particles passing a 50-mesh screen, one of them, No. 8989, now contained 37.65 per cent passing this screen. The relative proportion of all the sizes of particles have been changed materially, but a careful study of the results fails to reveal any explanation of the problem under discussion.

TABLE X.—*Grading of aggregate from cylinders after compression with percentage of voids in compressed cylinders*

No.	Sieve analysis.				Unfilled voids in cylinders.
	Retained on—			Passing 50-mesh.	
	10-mesh.	20-mesh.	50-mesh.		
Sand	20.65	24.90	41.80	12.65	23.9
10101	19.65	32.30	35.75	12.30	26.8
9093	13.90	28.75	36.50	20.85	26.1
10108	17.00	28.60	33.90	20.30	25.4
9445	14.00	30.55	35.95	19.50	23.2
9095	13.90	28.40	35.90	21.80	26.2
9094	14.25	30.65	40.73	14.35	25.8
8136	15.10	26.50	28.90	29.50	26.4
8992	16.05	27.75	37.70	18.50	25.5
9321	14.80	30.75	33.25	21.20	24.2
8993	15.40	28.65	41.05	14.90	27.7
8989	11.10	25.05	26.20	37.65	24.2
9281	17.00	26.50	31.75	24.75	21.0

The last column of Table X gives the calculated unfilled voids in each type of test piece. They represent the percentage difference between the actual specific gravity of the test pieces found by dividing their weight by their volume, and their ideal specific gravity calculated from the specific gravities and the percentage by weight of their constituents.

When it was found that no physical tests could be correlated directly with the behavior of the rocks in mixtures, it was suggested that the surface character and cleavage of the particles might be responsible for the differences. An examination with a hand glass seemed to show some interesting differences in surface character, and in order to permit a more careful investigation enlarged photographs of a few 10-mesh particles of each rock were made. Reproductions are shown in the accompanying plates. Plate 49 shows the first six rocks in Table VIII. These are of low average toughness and all fail to show any toughness with the light tar, except the biotite gneiss (9095) which gives a toughness of 1 at seven days. These rocks are large grained and made up of individual glassy particles, and therefore may be characterized as possessing smooth surfaces. This is most evident in the case of the sand, which had the lowest average toughness of any of the materials shown in Plate 49. In Plate 50 are shown fragments of the rocks which gave the relatively higher toughness values, except the sandstone (8136). It will be noted that the surface condition of these particles is quite different from those in Plate 49 on account of the fine-grained, relatively rough surface. The photograph of the feldspathic quartzite (9321) fails to show this character as clearly as desirable, but it can be stated that the fragments have a decidedly dull or frosted appearance, probably due to the feldspar content, as compared with the glassy quartzite (10108) in Plate 49. A comparison of the photographs with the toughness results would therefore seem to offer one explanation for the difference in the behavior of the various rocks, and these differences appear, to some extent at least, to be due to the fact that polished, glassy faces of the rocks in Plate 49 fail to hold the bitumen as well as the rougher surfaces of the rocks shown in Plate 50. An exception is noted in the case of the sandstone (8136) shown in Plate 50. The particles of this rock present a decidedly rough, dull surface, but the rock in combination with all bituminous materials showed the lowest average toughness of any tested, owing to the fact that the individual particles of the specimen were bound together loosely. In fact, the rock could be crumbled in the hand without very great difficulty. As noted above, a bituminous concrete section in which this rock was used failed rapidly and this was evidently due to the failure of the individual rock fragments rather than to the failure of the adhesion of the bitumen.

CONCLUSIONS

From the foregoing investigation and data the following conclusions may be drawn:

(1) The toughness of bituminous aggregates in which a given bituminous material is used will not be the same for every type of rock.

(2) Tests of laboratory specimens can be directly correlated with results in service.

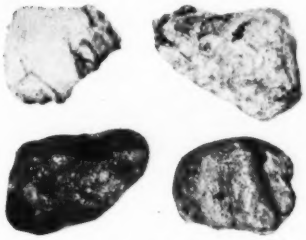
(3) The difference in behavior of the various rock types can not be directly attributed to any of the routine physical test values of the rock, but appears to be due largely to differences in the surface character of the rock particles.

(4) While relatively soft or fluid bitumens may yield satisfactory results in bituminous concrete with some types of rock, their use with other types will lead to failure of the road surface.

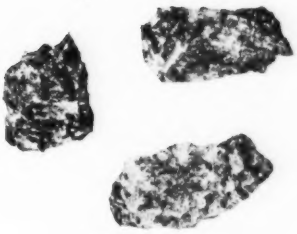
(5) The impact or toughness test of bituminous aggregates offers possibilities as a means of determining in advance the relative behavior in service of bituminous concretes. While the authors at this time have no definite recommendations to offer with regard to their last conclusion, it may be stated that further experiments will be made with that end in view.

PLATE 49

A.—Sand.
B.—Diabase (10101).
C.—Biotite schist (9093).
D.—Quartzote (10108).
E.—Biotite granite (9445).
F.—Biotite gneiss (9095).



A



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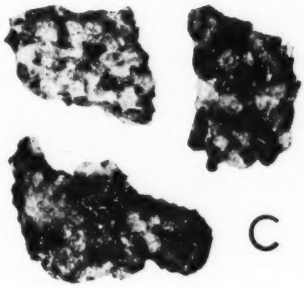

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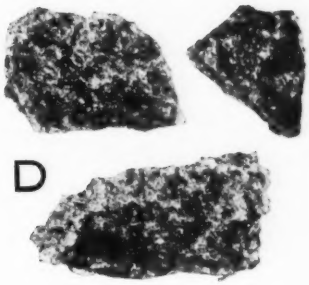

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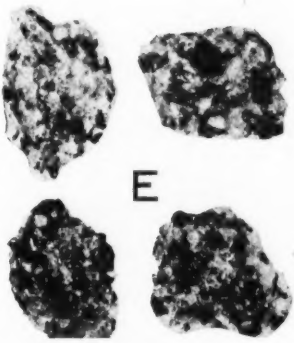

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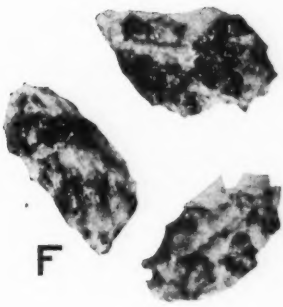

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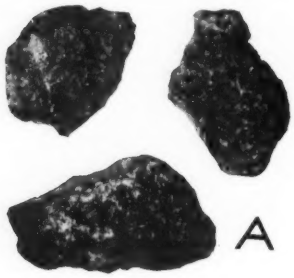
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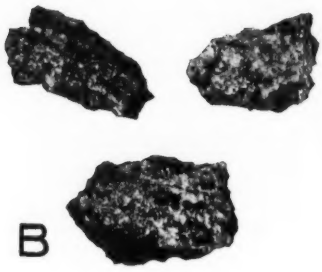
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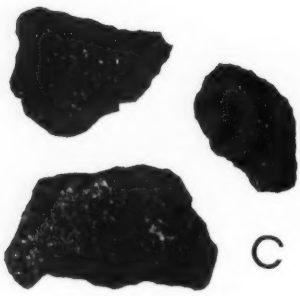
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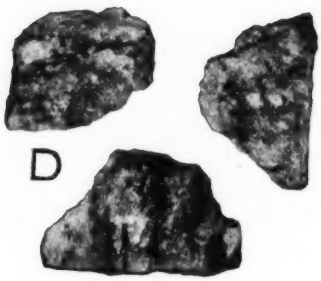
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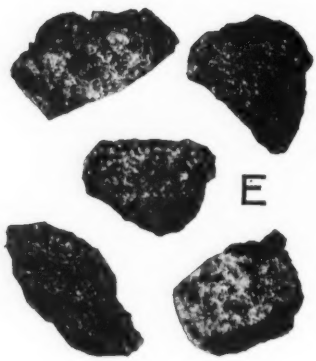
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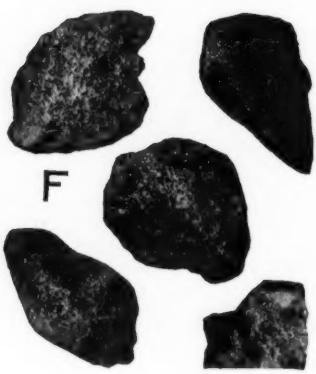
F

PLATE 50

A.—Altered diabase porphyry (9094).
B.—Feldspathic sandstone (8136).
C.—Open-hearth slag (8992).
D.—Feldspathic quartzite (9321).
E.—Chlorite schist (8989).
F.—Limestone (9281).

ORIGIN OF ALKALI

By ROBERT STEWART,[1] *Formerly Chemist*, and WILLIAM PETERSON, *Geologist, Utah Agricultural Experiment Station*

INTRODUCTION

The term "alkali" was probably first applied to the white incrustation on the dry arid plains by the hunters and trappers of the Far West long before the attention of the scientific man was directed to it. The term undoubtedly originated with them, because the wind carried fine white powder and deposited it in the dry parched mouth and nose of the traveler and seemed to increase the great distances between the watering places by this burning thirst and apparent caustic effect of the dry dust. The parched throat of the weary thirsty traveler felt as if it had been subjected to some caustic soda. Hence, the term "alkali" was applied to this white deposit. In addition, the early travelers and settlers of the Far West, being separated from the markets for caustic alkali, were forced to secure the alkali carbonates for soap making from the burning of the native bushes and trees such as greasewood, cedars, and pines. The analogy between the white deposits in the soil and the white caustic obtained from the ashes of vegetation was also possibly sufficient to the lay mind to cause the same term to be applied to both. Whatever the origin of the term, it has an unimportant chemical, but a very important agricultural, significance.

HISTORICAL REVIEW

The first record we have of its scientific investigation is in 1870. The Chemist to the Commissioner of Agriculture in his report (1, p. 96)[2] says:

> Dr. Edward Palmer brought to the laboratory from Western Kansas prairies a sample of what is called "alkali" of the western plains. It was in the form of a dry, milk-white powder, mixed with bleached leaves and coarse grass. It did not effervesce with acids, nor did it exhibit an acid reaction to test-paper. It contained:
>
> | | |
> |---|---|
> | Water | 3.6 |
> | Insoluble clay | 1.5 |
> | Chloride of sodium | traces. |
> | Sulphate of soda | 94.6 |
> | | 99.7 |

It is consequently a native sulphate of soda. There is no evidence to show that it is a product of volcanic action. It may owe its origin to the decomposition of sulphate

[1] Now Associate Professor of Soil Fertility, University of Illinois.
[2] Reference is made by number to "Literature cited," p. 353.

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of lime, which is largely present in the soils at the foot of the Rocky Mountains and Sierra Nevada series, by means of carbonate of soda occurring as efflorescences on soil. The usual origin of sulphate of soda is either directly from volcanic sources, or by the delivery of springs containing salt derived from preexisting sedimentary beds. In a few cases it is derived from the oxidation of sulphur in bituminous strata, or in pyritiferous beds which, reacting on common salt, produce thenardite or other forms of sodic sulphate.

In 1876 the East India Government on petition appointed a committee to investigate and report on the increasing encroachments of "reh," a saline efflorescence on soil irrigated by canals. One member of this committee, Mr. Medlicott, Superintendent of the Geological Survey of India, says (6), regarding the origin of "reh":

> Every one seems content to accept the reh as an ultimate fact—that there it is—as much an original ingredient of the ground as the clay and sand. Now, I consider it demonstrated that this view is false, and that an origin is assignable for reh which introduces the gravest apprehensions as to the possible results of canal irrigation. The present chief store of reh is in the saline subsoil-water—the upper water-bed found more or less all over Upper India. Beneath this, at depths of from sixty to one hundred feet, sweet water is found, containing no more salt than the canal water, which is very pure. Now, I consider it certain that these upper deposits were originally as free from those salts as is now the alluvium of the delta; and that the present state has been brought about in the course of generations, slowly but with increasing rapidity, owing to the total subversion of the natural climatal conditions, chiefly by the total destruction of forest vegetation. The explanation is simple: every soil contains some reh, and all percolation water from soils is also contaminated by those salts, which are the refuse products (the parts unassimilated by vegetation) in the very slow process of formation and consumption of soil. Unless removed it must accumulate; and the natural process of purification is a certain necessary amount of percolation and ground drainage, the pure rain-water passing through the soil carrying off any injurious excess of these rejected salts. If the washing process is sufficiently free to insure a certain discharge of this percolation water by natural subsoil drainage, there will be a constant dilution and removal of the subsoil-water; but if the percolation through the soil is no more than to restore what has been dissipated by capillary action and evaporation during the dry season, the reh will go on accumulating in the upper water-table; and such has been the condition of Upper India for many a day.

Hilgard, soon after the beginning of his association with the University of California in 1874, began his classical work upon the various phases of the alkali problem. In his report to the president of the university in 1877, he says (5, p. 43), in a discussion of the origin of alkali:

> The immediate source of the alkali is usually to be found in the soil water, which, rising from below and evaporating at the surface, deposits there whatever of dissolved matters it may contain.

And the manner in which it gets its way into the soil water is fully discussed in the numerous subsequent publications on the subject by him and possibly is fully represented by the following direct quotation (6, p. 9):

> The same alkali salts are formed everywhere in the world; but in countries having abundant rainfall they are currently washed, as formed, into the country drainage, while in regions where rainfall is deficient, the scanty moisture only carries them a

little way down into the subsoil, from which they rise to the surface by the evaporation of the water, and are thus accumulated at, and close to, the very top of the soil, often in the form of crusts or crystals. It is right there that nearly all the damage is done; the water in the depths of the soil is very rarely strong enough to hurt the roots of plants, directly.

These direct quotations probably will represent the teachings of Hilgard regarding the origin of the alkali of arid soils.

Hilgard also emphasized the necessity of care in the use of saline irrigation waters (6, p. 41), which may intensify the alkali condition of the soil.

Many of the Experiment Stations of the West have published bulletins and reports dealing with the alkali question, but they have simply adopted Hilgard's conception of the origin of alkali and present no new views on the question.

A notable exception is found in the work of Buffum, who suggests a different origin (2, p. 219). He says:

In the Wheatland district, although the rainfall is too small to produce crops, and all farms are irrigated, no injurious alkali has appeared upon any of the uplands under cultivation. *The soil of the uplands here is colluvial and derived from earlier geological formations which do not supply the alkali salts.*

This view was further advocated by Slosson (8, p. 40):

The principal source of the alkali is not, however, the water used in irrigation, but the beds of soluble salts that are deep in the soil. As soon as water is put on the land these salts are drawn to the surface by evaporation.

Soon after the organization of the Bureau of Soils of the United States Department of Agriculture its attention was directed to the alkali problems of the West. Regarding the origin of alkali in certain soils at Billings, Mont., Whitney and Means (11, p. 35) say:

The results of these investigations show that the ultimate source of the alkali is in the sandstone, and particularly in the shale or slate rocks from which the soils have been derived.

It is, however, not clear as to the condition in which they occur or the manner of the transfer to the soils. Fortunately in a later publication (4, p. 10) of the Bureau additional information is furnished upon this point.

In a few cases the genesis of alkali can be clearly traced. For instance, in the Billings area, Montana, * * * it seems obvious that the source of the material is found in the sulphides of iron prevalent in the Fort Benton shales, which on exposure to the air oxidize to the sulphates and then on contact with water hydrolyze, forming sulphuric acid and ultimately the sulphates of the alkalies and alkaline earths.

Various other theories are also discussed regarding the origin of alkali, such as deposition from wind-blown spray and Cameron's (4, p. 11) conception of the derivation of alkalies by means of hydrochloric and sulphuric acid resulting from the weathering of the original rock, which, as Clarke shows (3, p. 17), contains an average of 0.07 per cent of chlorin

and 0.108 per cent of sulphuric acid. Regarding the conception of the derivation from preexisting geological deposits, Dorsey (4, p. 10) says:

> In some cases it may be regarded as fairly evident that the salts do come from more or less deep-seated deposits resulting from the desiccation at more or less remote periods of time of bodies of sea water. In many cases, however, there is a total lack of confirmatory geologic evidence, and this explanation must be regarded as very unsatisfactory.

It may thus be seen that there are a number of theories proposed regarding the origin of "alkali" of the arid regions. The following are some of the most important: (1) Derivation from gypsum by action of sodium carbonate, as proposed by Antisell; (2) accumulation of the unused portion of the soil or refuse, as proposed by Medlicott; (3) Hilgard's conception of the formation of soluble salts in the soil by ordinary process of weathering and their concentration in the lower depths by the action of the limited rainfall; (4) Whitney and Means's conception of their formation by oxidation of the sulphids of the shales; (5) Buffum's view of the presence of isolated deposits or lakes of the alkali salts in the country rock; (6) Cameron's theory regarding the formation of hydrochloric and sulphuric acid from the chlorin and sulphur content of the country rock and the subsequent leaching action of these acids on the insoluble silicates of the soil or rock; and (7) the deposition by wind spray from sea water.

THE PROBLEM

Our attention was directed forcibly toward the alkali problem in connection with our investigation regarding the origin of the "niter spots," a special phase of the more general alkali problem.

The results of these investigations, which have been presented elsewhere (9), led us to a very definite conception regarding the origin of alkali in at least a large portion of Utah, Colorado, Wyoming, Montana, Alberta, Canada, and undoubtedly in many other areas of the arid region. The preponderance of evidence submitted by us clearly demonstrates that the "niter spots" are the direct result of the leaching action of water upon the nitrates preexisting in the country rock and their concentration at the points of greatest evaporation. The nitrate accumulations are always accompanied by the other water-soluble so-called alkali salts. The facts led us to formulate a definite hypothesis regarding the origin not only of the nitrates themselves but also of the other salts as well.

The hypothesis upon which the following work was based is: The "alkali" is derived from the soluble salts preexisting in the country rock of the observed area. This country rock rich in alkali not only contributes to the soil formation but is adjacent to and underneath the agricultural soils of the affected areas. The original soil may not have sufficient salts present to prevent crop production, but upon the application of the irrigation water the alkali salts existing in the country

rock are leached out and concentrated in the surface soil. Leaky irrigation canals and the rise of the ground-water table give greatest and quickest concentrations.

GEOLOGIC FORMATIONS

Field studies were made of the area during the years 1913 and 1914, when some 400 representative samples of sandstone, shale, alkali, clay, and ash[1] were collected and later submitted to complete "alkali" analysis. The data of the nitric and potassium content have been presented and discussed elsewhere (9, 10).

The geological evidence shows that during the Cretaceous and the Tertiary periods shallow seas covered the eastern part of Utah, western Colorado, western Wyoming, eastern Idaho, and extended north through Montana into Canada (9, map). This is not the whole area covered, but the part given special study in this paper. The Lower Cretaceous is wanting, and the Upper Cretaceous lies unconformable on the Jurassic deposit. The climate during the Jurassic was arid, as is evidenced by the great areas of red sandstone containing rock salt and great quantities of gypsum. During the Lower Cretaceous the area was land and suffered erosion. The divisions of the periods in general are as follows:

Arrangement of geologic formations

Tertiary	Eocene	Green River formation, Wasatch, Fort Union.	Light-colored sandstone, limestone, and shale with beds of rhyolitic ash and lenses of salt and gypsum. Coal beds and layer of dark-colored shale. Forms floor of Uintah Basin.	
Upper Cretaceous	Montana	Mesaverde	Alternating layers of buff sandstone and shale with beds of workable coal near base.	2,000–4,000 feet in thickness.
	Colorado	Mancos	Black and blue-gray shale with light-colored sandstone near top.	1,000–3,000 feet in thickness.
		Dakota	Buff sandstones, highly colored shale with carbonaceous shale and some coal at the base.	300–2,500 feet in thickness.
Unconformity.				
Jurassic		Brown-, yellow-, and red-colored sandstone with lenses of limestone and gypsum.		500–2,000 feet in thickness.

When the sea again covered the land at the end of Lower Cretaceous times, conglomerates, sandstone, and shale were deposited; and during the Upper Cretaceous the sea continued to deepen during the period of deposition. But at times the sea was shallow, forming layers or salty marshes in which gypsum and salt were deposited. The shales of the Mancos, which are more than 2,000 feet thick in places, contain beds which are heavily impregnated with gypsum, sodium sulphate, and some sodium chlorid. The deposit is not uniform, but appears in certain beds irregularly distributed through the deposit.

[1] A term which was chosen to apply to a mixture of dry dust with crystals of alkali found just under the clay crust on the most affected parts.

The Mesaverde contained much colored sandstone and the coal deposit of the period. The sandstone shows much cross-bedding, marks, etc., indicating shallow water deposits.

The sea partially disappeared at the end of the Mesaverde, so the Tertiary strata lies unconformably on it over large areas. The climate of the Tertiary was similar to the Upper Cretaceous, and much of the material deposited in the Tertiary seas was derived from the weathered Cretaceous. The salts in the shallow seas seem to have their origin in the concentrating of sea waters encroaching on the land.

It is out of this material, heavily impregnated with the alkali salts, that many of the soils of the arid West are formed. The climate continued to be arid, and the salts deposited with the shale and sandstone in a widely disseminated form have been protected from leaching not only by the limited rainfall of the area but also by the impervious covering of plastic clay resulting from the weathering of the shale.

METHOD OF ANALYSIS

The ground-up rock or soil was extracted with pure distilled water in the ratio of 1 part of fine-ground rock to 20 parts of water. Usuallly whenever the quantity of rock would permit, 100 gm. of the rock material was treated with 2,000 c. c. of water for eight hours in a shaking machine. The extract was then filtered through a Chamberland-Pasteur filter by means of compressed air.

The soil extract was analyzed for total salts, calcium, magnesium, carbonic acid, sulphuric acid, chlorin, potassium, and nitric nitrogen. The methods of analysis, except for nitric nitrogen, were essentially those of the Association of Official Agricultural Chemists[1] for alkali waters. Owing to the high content of chlorin, the aluminium reduction method as proposed by Moore (7) was used for the determination of nitrates as follows: 200 c. c. of the soil extract were boiled down to small volume to expel all free ammonia. The solution was then transferred to 125 c. c. test tubes, and 2 c. c. of strong sodium hydroxid and about 1 gm. of aluminium foil added. The tube was then fitted with one-hole rubber stopper containing a tube drawn out to a capillary. The reduction was allowed to go on at about 21° to 22° C. for about 12 hours. The solution was then transferred to a 500-c. c. Kjeldahl flask, 150 c. c. of ammonia-free water added, the ammonia distilled into standard sulphuric acid (*N*/30), and the excess titrated against standard alkali (*N*/30), using lacmoid as an indicator.

SOLUBLE SALTS IN CRETACEOUS SANDSTONE

Twelve samples of Cretaceous sandstone were collected and analyzed for water-soluble salts; the results are recorded in Table I as pounds per 2,000,000 of sandstone. The results are arranged in the table in the order of the highest nitric-nitrogen content.

[1] WILEY, H. W., ed. EXTRACTS FROM THE PROCEEDINGS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1909. U. S. Dept. Agr. Bur. Chem. Circ. 52, 32 p. 1910.

TABLE I.—*Soluble salts in Cretaceous sandstone*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
260A	Thompson, Utah	1,042	280	1,040	461	Trace.
73	Grand Junction, Colo.	48,120	38,880	880	106,744	2,552
80	do	3,074	2,257	333	31,710	1,300
292	Vernal, Utah	160	768	480	1,216	Trace.
81	Grand Junction, Colo.	802	1,384	383	5,980	2,127
279	Vernal, Utah	1,202	769	600	1,514	Trace.
88	Green River, Utah	1,470	276	350	4,829	Do.
290	Vernal, Utah	1,042	629	640	2,503	Do.
242	Superior, Wyo	802	943	640	1,136	Do.
244	do	1,058	1,835	1,480	19,360	1,701
245	do	1,604	1,694	1,200	1,218	567
241	do	802	2,237	720	494	567
Average	Cretaceous	5,098	4,329	729	14,764	170

All the samples of Cretaceous sandstone contain appreciable quantities of soluble salts and are especially rich in sulphates with appreciable quantities of carbonic acid and chlorin, and, as already reported, they all contain nitric nitrogen. From the analytical data reported above, the probable chemical combination may be calculated in any manner desired. Some such calculations have been made in the manner suggested by the Association of Official Agricultural Chemists.

On this basis of calculation, with the average results reported above, all the carbonates, sulphates, chlorids, and nitrates present in the Cretaceous sandstone consist of calcium and magnesium compounds. There remains also a slight excess of magnesium after these acid ions are satisfied, which undoubtedly represents that united with the phosphoric and silicic acids. These soluble salts undoubtedly exist in the rock in the crystalline form with water of crystallization; but the amount of this water of crystallization was not determined, the results being simply calculated to the anhydrous basis. There is present in these sandstones, therefore, 983 pounds of calcium bicarbonate [$Ca(HCO_3)$], 16,469 pounds of calcium sulphate, 3,922 pounds of magnesium sulphate, 985 pounds of magnesium chlorid, and 1,961 pounds of magnesium nitrate—that is, over 1.21 per cent of the sandstone consist of these soluble salts. The leaching of such rock by the irrigation and ground water must result in a concentration of these salts where the seepage or ground water approaches the surface. The concentration of such soluble salts of calcium and magnesium will bring about double decomposition with the formation of soluble salts of sodium, such as the chlorid and sulphate. However, it must be remembered that the sandstone and shale may and do become mixed in the soil formation in some areas. The soil derived entirely from the sandstone, however, should not contain such an excess of soluble salts of a harmful nature as to be destructive to crop growth. There may be and undoubtedly are other reasons why the alkali problem is not

so vital in the sandy soils of the area, but the fact that the salts in the sandstone are largely the salts of calcium and magnesium is one important reason.

SOLUBLE SALTS IN CRETACEOUS SHALE

Fifty-seven samples of Cretaceous shale were collected and analyzed for soluble salts. The results are recorded in Table II as pounds per 2,000,000 of shale.

As an average, the Cretaceous shale is much richer in sulphates and chlorids than is the sandstone. Again, the sulphates are the predominating salts. There is little less calcium in the shale than in the sandstone, while the latter contains over twice as much magnesium as the former. The increase in sulphates and chlorids is due to the presence of the salts of sodium.

As an average, there are present in this shale 993 pounds of calcium bicarbonate, 15,738 pounds of gypsum, or calcium sulphate, 10,780 pounds of magnesium sulphate, 13,036 pounds of sodium sulphate, 1,148 pounds of sodium chlorid, and 2,079 pounds of sodium nitrate—that is, at least 2.19 per cent of this shale material consist of water-soluble salts. Some samples are markedly rich in the soluble salts, while others are not so rich. But all the samples contain some soluble salts, and, unlike the sandstone, the shale contains large quantities of the more harmful sulphate and chlorid of sodium.

There is, of course, a marked variation in the composition of the soluble salts. In some samples there is no soluble calcium, while in others there is no soluble magnesium. In one sample there are no soluble carbonates, but the solution is really acid. Many samples contain no chlorin, or at least only traces of this acid ion.

There is no definite ratio between the various acidic or basic elements in the several samples. The sample which is richest in chlorids, No. 84 from Green River, contains only moderate amounts of sulphates. It is much richer in calcium than the average, but is not the richest in calcium. It contains less than the average amount of magnesium and nearly the average amount of carbonic acid. It contains nearly the maximum amount of nitric nitrogen, yet there are other samples of shale which are richer in nitric nitrogen but which contain only traces of chlorin. The sample which is richest in sulphate, No. 8126 from Emery, Utah, contains only traces of chlorin, no carbonic acid, moderate amounts of calcium and magnesium. The 12 per cent of soluble sulphates consist largely of the compounds of magnesium and sodium. This sample is a coal-bearing shale, the definite strata of coal being seen with the naked eye. It was obtained just below an economic supply of undeveloped coal near Emery, Utah. Its aqueous solution was highly colored a dark brown. This lack of any definite ratio is exactly what one would expect. The salts were deposited from the saline water of the old inland seas, and isolated playas would undoubtedly become more concentrated in some salts than others

TABLE II.—*Soluble salts in Cretaceous shale*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_3).	Chlorin (Cl).
68	Grand Junction, Colo.	7,699	3,154	480	46,408	567
294	Vernal, Utah	481	978	240	1,342	302
274	Thompson, Utah	1,042	961	1,280	6,321	2,556
264	do	13,152	6,220	800	101,400	Trace.
79	Grand Junction, Colo.	5,948	4,135	300	42,800	Do.
261	Thompson, Utah	1,388	1,083	680	44,904	425
69	Grand Junction, Colo.	1,609	13,276	320	25,016	213
84	Green River, Utah	9,960	699	666	44,110	7,562
86	do	802	219	667	7,530	2,009
123	Emery, Utah	722	Trace.	1,440	20,080	709
89	Green River, Utah	3,743	335	383	28,580	235
65	Grand Junction, Colo.	3,369	358	240	15,669	None.
98	Price, Utah	2,004	205	533	11,180	236
75	Grand Junction, Colo.	5,133	8,247	640	42,800	None.
262	Thompson, Utah	4,331	4,736	760	44,216	284
78	Grand Junction, Colo.	21,488	3,215	560	74,536	Trace.
66	do	1,122	716	1,000	22,154	284
281	Vernal, Utah	1,090	419	1,560	2,304	284
289	do	1,765	524	960	571	Trace.
102	Price, Utah	2,606	Trace.	533	12,840	Do.
130	Emery, Utah	11,398	1,049	760	63,967	284
95	Price, Utah	2,810	873	466	17,120	118
100	do	1,470	Trace.	700	1,936	Trace.
67	Grand Junction, Colo.	11,660	1,464	300	26,504	567
144	Emery, Utah	320	752	1,280	6,748	284
85	Green River, Utah	8,754	495	367	31,650	Trace.
83	Grand Junction, Colo.	10,893	7,241	200	61,960	Do.
90	Price, Utah	None.	516	433	9,742	Do.
97	do	1,938	Trace.	500	12,896	Do.
286	Vernal, Utah	1,764	978	720	103,360	Do.
76	Grand Junction, Colo.	6,738	2,796	780	37,600	Do.
110	Orangeville, Utah	2,967	1,552	560	11,728	284
99	Price, Utah	2,049	Trace.	200	16,874	Trace.
108	Castledale, Utah	5,453	Do.	600	27,032	213
287	Vernal, Utah	1,684	786	600	39,768	Trace.
105	Castledale, Utah	1,524	Trace.	760	2,370	284
63	Grand Junction, Colo.	8,260	716	260	21,428	284
64	do	10,988	349	300	26,992	284
116	Emery, Utah	10,824	1,136	280	21,104	Trace.
119	do	3,047	718	540	8,876	Do.
91	Price, Utah	301	437	566	3,512	1,359
291	Vernal, Utah	962	961	360	2,338	Trace.
268	Uintah, Utah	1,042	974	1,080	1,876	Do.
113	Orangeville, Utah	8,100	2,788	1,080	33,912	425
269	Uintah, Utah	1,604	1,031	1,594	2,864	Trace.
S126	Emery, Utah	4,009	29,188	None.	256,400	Do.
271	Uintah, Utah	1,203	1,066	1,080	1,251	None.
120	Emery, Utah	10,986	585	560	47,472	425
122	do	2,726	Trace.	640	22,976	567
117	do	642	Do.	2,120	28,440	142
107	Castledale, Utah	15,756	Do.	1,600	184,720	16,872
71	Grand Junction, Colo.	1,042	11,184	440	12,472	Trace.
270	Thompson, Utah	1,123	908	840	790	None.
280	Vernal, Utah	386	577	2,040	1,284	Do.
278	do	882	629	1,920	2,238	426
128	Emery, Utah	802	1,695	840	30,320	Trace.
Average	Cretaceous	4,898	2,156	728	28,159	675

This shale, so highly impregnated with the sulphates, chlorids, and nitrates of calcium, magnesium, sodium, and potassium, is the sole material out of which many of the soils of the area are made. In certain small areas the sandstone, also rich in soluble salts, contributes to the soil formation, while in still other small areas the river wash from other geological horizons contribute to the soil formation. But the major portion of the land of the area investigated is derived from the Mancos shale of Cretaceous origin. The irrigating canals of the region, run by gravity, are diverted from the rivers high up on the stream and, as a result, cut through the shale strata in many places. The shale, broadly speaking, is nearly horizontal, and the strata lie like the leaves of a book. The irrigation canal cuts this strata in the higher-lying ground, and, as a result, the seepage water from the canal follows the folds of the shale to the point of outcrop where the soluble salts, concentrated from the entire shale area covered, are deposited on evaporation of the water. The result is a good crop of alkali or an alkali bog. In certain isolated basins the problem is intensified by the rise of the ground water, with its solvent action upon the undecomposed shale. This is the sole origin of the alkali of the observed area.

SOLUBLE SALTS IN THE CRETACEOUS ASH

As already reported, there appears on the surface of the slight decomposed shale a mealy mass of white-gray material which has a burnt-ash-like appearance. The material is crystalline when examined with a hand lens. On placing under the microscope for examination, it largely dissolves on the addition of water. Eight representative samples of this were collected and analyzed. The results are recorded in Table III.

TABLE III.—*Soluble salts in Cretaceous ash*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_3).	Chlorin (Cl).
133	Emery, Utah	11,308	3,552	5,200	129,680	5,389
77	Grand Junction, Colo.	12,192	10,206	240	255,200	1,418
124	Emery, Utah	722	Trace.	1,040	44,568	900
260	Thompson, Utah	19,808	978	840	114,600	852
276	Vernal, Utah	7,377	3,600	640	127,960	709
134	Emery, Utah	Trace.	559	9,600	14,416	Trace.
145	do	6,576	4,662	880	102,800	1,276
122a	do	1,764	Trace.	1,240	71,408	709
Average	Cretaceous	7,468	2,807	795	93,193	1,400

This ash material found on the surface of the shale represents the accumulation of salts due to the solvent leaching and evaporation of rain or ground water.

The soluble carbonate in the ash is nearly the same as in the shale, while the magnesium has slightly increased. The calcium has nearly doubled, while the chlorin has more than doubled. The sulphates have increased by over three times. There are 1,073 pounds of calcium bicarbonate present, 21,743 pounds of calcium sulphate, 14,035 pounds of magnesium sulphate, 99,910 pounds of sodium sulphate, 2,380 pounds sodium chlorid, and 3,623 pounds of sodium nitrate—that is, in this ashlike material the concentration of salts has become such that 7.13 per cent of the total material consist of the sulphates, chlorid, nitrates, and carbonates of calcium, magnesium, sodium, and potassium. This accumulation has been brought about in the virgin native condition by the concentrating action of the limited rainfall. It is strongly indicative of the more intensive action which may be brought under the irrigated conditions due to the leaky irrigation ditch and the rise of the ground water.

SOLUBLE SALTS IN THE UNCULTIVATED SOIL AND CLAY

Twelve samples of the clay or soil resulting from the weathering of the shale in place were collected and submitted to analysis. This clay or soil has never been cultivated and does not even support a virgin crop of grass or weeds. These samples are fairly representative of the kind of soil formed in place from the shale. The results are recorded in Table IV.

TABLE IV.—*Soluble salts in uncultivated soils and clay*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_3).	Chlorin (Cl).
277	Vernal, Utah	51,328	1,887	1,120	58,040	2,410
263	Thompson, Utah	4,973	2,132	760	36,376	Trace.
87	Green River, Utah	4,812	233	383	15,968	599
131	Emery, Utah	8,829	839	800	43,744	425
96	Price, Utah	7,953	1,019	400	28,090	Trace.
85	Green River, Utah	8,754	495	367	36,184	Do.
146	Emery, Utah	5,694	7,656	920	112,880	4,253
121	do	8,260	525	620	34,704	284
125	do	1,363	Trace.	920	36,672	Trace.
143	do	160	769	1,200	9,480	3,800
Average	Cretaceous	5,593	1,556	749	41,213	1,176

The amount of calcium in the clay is slightly higher than in the shale, while the magnesium is slightly less. The carbonic acid is practically constant in the shale and clay. The sulphuric acid has materially increased, as has also the chlorin.

As an average, there are 1,021 pounds of calcium bicarbonate in the clay, 18,091 pounds of calcium sulphate, 7,780 pounds of magnesium sulphate, 9,411 pounds of sodium sulphate, 1,999 pounds of sodium

chlorid, and 775 pounds of sodium nitrate. Again, the predominating acid ion is the sulphate, followed closely by chlorin—that is, this uncultivated clay contains 1.75 per cent of water-soluble salts and over one-half of the salts consists of sodium and magnesium sulphates. Is it any wonder that these clay hills do not support any native vegetation? Such a soil when underlain by the characteristic ash reported above is certainly too concentrated for the most resistant crops.

"ALKALI" OF CRETACEOUS ORIGIN

As already reported, characteristic alkali spots occur in the native condition in the uncultivated clay hills wherever moisture conditions are such as to bring about a concentration of the water-soluble salts of the shales or sandstones. These alkali spots may be found near springs or bogs in these hills. Twenty-three samples of such alkali were collected and analyzed for soluble salts. This alkali has no connection with irrigation canals. The results, which show enormous accumulations of soluble salts in these native alkali spots, are recorded in Table V.

TABLE V.—*Soluble salts in the "alkali" of Cretaceous origin*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_3).	Chlorin (Cl).
132	Emery, Utah	13,712	11,016	None.	371,920	16,304
77	Grand Junction, Colo.	12,192	None.	240	255,200	1,418
275	Thompson, Utah	19,408	597	1,360	76,080	567
94	Price, Utah	10,960	29,840	1,632	182,280	2,670
72A	Grand Junction, Colo.	9,945	111,840	4,720	103,500	3,686
127	Emery, Utah	8,018	58,016	920	58,144	11,416
114	Castledale, Utah	7,779	86,480	2,640	5,517	50,192
101	Price, Utah	10,426	21,888	1,500	207,040	6,145
295	Vernal, Utah	8,100	2,045	600	226,800	Trace.
82	Grand Junction, Colo.	5,948	5,126	517	44,048	None.
137	Emery, Utah	22,456	2,255	240	44,780	5,246
129	do	4,571	8,760	4,440	61,160	2,694
112	Orangeville, Utah	12,188	35,652	2,240	467,360	33,320
282	Vernal, Utah	2,807	1,136	29,160	189,440	11,485
70	Grand Junction, Colo.	15,078	88,200	20,800	903,360	12,336
109	Castledale, Utah	17,963	Trace.	3,040	310,720	31,760
103	Price, Utah	14,840	29,810	1,300	275,500	3,345
136	Emery, Utah	23,420	612	800	56,848	587
72	Grand Junction, Colo.	4,892	8,424	480	65,776	284
126	Emery, Utah	802	Trace.	920	1,448	None.
118	Rochester, Utah	7,777	4,710	2,520	197,440	32,328
111	Orangeville, Utah	15,960	52,136	1,200	352,800	2,269
115	Castledale, Utah	12,429	26,652	1,720	263,360	12,052
Average...	Cretaceous	11,376	25,447	2,533	245,805	10,391

These virgin alkali spots are especially rich in sulphates of magnesium and sodium. Calculations as before show that there are 3,419 pounds of calcium bicarbonate, 35,666 pounds of calcium sulphate, 127,235 pounds of magnesium sulphate, 152,682 pounds of sodium sulphate, 17,665

pounds of sodium chlorid, and 5,492 pounds of sodium nitrate per 2,000,000 pounds as an average of 23 determinations of alkali from widely separated portions of the Cretaceous area—that is, in this crude alkali material collected in the uncultivated soil there is 17.10 per cent soluble in water.

In our previous publications (9, 10) attention was called to the fact that the niter spots were not characteristic of cultivated irrigated soil, but were found in the virgin condition wherever the moisture condition was suitable for a concentration of the salts. Special attention was directed to one such spot, as represented by samples 130, 131, 132, and 133, representative of the shale, soil, alkali, and ash, respectively. Now that the complete data are available, it is interesting and instructive to study these samples again. The complete data are given in Table VI.

TABLE VI.—*Soluble salts in material from a native niter spot*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Sample.	Calcium bicarbonate.	Calcium sulphate.	Magnesium sulphate.	Sodium sulphate.	Sodium chlorid.	Sodium nitrate.
130	Shale	1,026	37,508	5,240	49,962	483	899
131	Clay or soil	1,080	29,066	4,195	29,807	723	768
132	Alkali	None.	46,620	55,080	442,407	297,168	67,080
133	Ash	7,020	32,259	12,760	130,051	8,161	65,380

In this characteristic niter spot occurring in the virgin soil we find that the accumulations of nitrates are accompanied by accumulations of other soluble salts such as the chlorids and sulphates of calcium, magnesium, and sodium. The parent shale contains 4.75 per cent of soluble salts, over one-half, or 52.4 per cent, of which is sodium sulphate; 10 per cent of calcium bicarbonate; 0.51 per cent of sodium chlorid; 0.94 per cent of sodium nitrate. In the soil derived from this shale there are 3.23 per cent of soluble salts in which the sulphates of sodium and calcium are about equal—that is, 45.4 per cent is sodium sulphate, 44.2 per cent is calcium sulphate, 8 per cent magnesium sulphate, 1.65 per cent calcium bicarbonate, 1.10 per cent sodium chlorid, 1.17 per cent sodium nitrate. In the alkali there are 45.5 per cent of total soluble salts with a marked increase in the chlorid, sulphur, and nitrate of sodium. Of the total soluble material 48.6 per cent is the sulphate of sodium, 32.1 per cent is the chlorid of sodium, 7.4 per cent is the nitrate of sodium, 6.05 per cent is the sulphate of magnesium, 5.13 per cent is the sulphate of calcium, while the bicarbonate of calcium is entirely missing. In fact, the aqueous extract of the alkali is acid to methyl orange. The ash contains 12.78 per cent of soluble salts, of which 50.9 per cent is the sulphate of sodium, 12.6 per cent is the sulphate of calcium, 5 per cent is the sulphate of magnesium, 25.5 per cent is the nitrate of

sodium, 2.8 per cent is the bicarbonate of calcium, 3.2 per cent is the chlorid of sodium. For convenience these results are brought together in Table VII.

TABLE VII.—*Percentage composition of alkali obtained from shale, soil, and ash*

Field No.	Sample.	Calcium bicarbonate.	Calcium sulphate.	Magnesium sulphate.	Sodium sulphate.	Sodium chlorid.	Sodium nitrate.
130.....	Shale.....	1.0	39.4	5.5	52.4	0.5	0.9
131.....	Soil.....	1.7	44.2	8.0	45.4	1.1	1.2
132.....	Alkali.....	.....	5.1	6.1	48.6	32.1	7.4
133.....	Ash.....	2.8	12.6	5.0	50.9	3.2	25.5

This characteristic niter spot is abundantly supplied with the sulphates of calcium, magnesium, and sodium. The proportion of the bicarbonate and magnesium sulphate varies but little. The chlorid and nitrate increase from a small proportion in the shale to relatively large amounts in the ash and alkali. The origin of the nitrate, as well as the other salts in the clay, ash, and alkali, is definitely traceable to the alkali-salt content preexisting in the shale itself. The color of the brown alkali is due to the old organic matter of the shale, which in this case lies immediately beneath economic coal deposits occurring in the shale.

SOLUBLE SALTS IN TERTIARY SANDSTONE

The samples of Tertiary sandstone collected represent widely separated portions of the Tertiary deposits. Owing to the lack of material, not all the samples reported in Utah Bulletin 134 (9) have been analyzed. The Tertiary sandstone is not so rich in alkali salts as is the Cretaceous sandstone. The results for the four representative samples is recorded in Table VIII as pounds per 2,000,000 of sandstone. There is less of all material in this sandstone except chlorin.

TABLE VIII.—*Soluble salts in the Tertiary sandstone*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Sulphuric acid (SO_4).	Carbonic acid (CO_3).	Chlorin (Cl).
273.....	Uinta Basin, Utah...	2,085	1,223	4,543	760	851
283.....	Lyman, Wyo.....	1,042	2,830	4,806	840	3,403
312.....	Utahn, Utah.....	410	760	395	800	Trace.
203.....	Millburn, Wyo.....	1,532	786	1,415	3,240	Do.
Average...	Tertiary.....	1,265	1,400	2,790	1,410	1,064

There is only 0.5 per cent of soluble salts present in the sandstone, which is about equally divided between the various salts of calcium and

magnesium. As in the Cretaceous sandstones, the sodium salts are entirely absent. There are 1,904 pounds of calcium bicarbonate present in 2,000,000 of sandstone, 2,621 pounds of calcium sulphate, 1,175 pounds of magnesium sulphate, 1,426 pounds of magnesium chlorid, and 2,530 pounds of magnesium nitrate. Again, there is a slight excess of magnesium which, no doubt, is united with phosphoric and silicic acids. The soluble salts in the sandstone amount to 0.45 per cent. The results of the analysis of the Tertiary shales are recorded in Table IX.

TABLE IX.—*Soluble salts in Tertiary shales*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
30	Richfield, Utah	54,920	5,680	1,200	13,252	12,052
310	Utahn, Utah	722	1,267	1,080	5,235	8,706
236	Lyman, Wyo	722	262	1,200	1,580	8,224
31	Sigurd, Utah	25,904	3,503	480	60,800	35,876
308	Utahn, Utah	722	1,468	1,480	1,646	2,797
300	Myton, Utah	6,576	646	480	923	20,704
232	Lyman, Wyo	561	873	2,840	9,944	7,656
299	Myton, Utah	160	960	2,000	1,811	2,326
223	Lyman, Wyo	1,600	489	1,600	7,572	711
307	Myton, Utah	241	1,136	3,120	1,877	284
304	do	321	314	1,640	5,531	681
233	Lyman, Wyo	4,813	786	920	4,974	2,269
36	Sigurd, Utah	5,936	2,009	320	1,409	2,474
305	Myton, Utah	160	262	600	1,908	1,702
215	Millburn, Wyo	240	411	2,480	3,720	284
222	Lyman, Utah	5,133	856	640	37,828	709
229	do	481	507	1,720	1,086	1,418
208	Millburn, Wyo	1,764	1,223	800	6,058	850
272	Vernal, Utah	882	873	3,000	4,280	Trace.
205	Millburn, Wyo	3,849	1,800	6,400	16,296	567
210	do	21,412	3,512	760	67,984	567
33	Sigurd, Wyo	1,042	None.	800	2,204	Trace.
211	Millburn, Wyo	321	do	880	None.	Do.
212	do	401	do	2,080	Trace.	142
213	do	321	do	2,720	None.	Trace.
306	Myton, Utah	2,406	1,380	800	71,800	Do.
32	Sigurd, Utah	642	363	320	3,391	Do.
39	Richfield, Utah	962	114	580	699	213
214	Lyman, Wyo	560	None.	720	None.	Trace.
Average	Tertiary	7,316	1,058	1,307	18,341	4,603

A comparison of these shales with the Cretaceous shales brings out a number of interesting points. Less magnesium and more chlorin is found in the shales of Tertiary origin, and there is more calcium and carbonic acid and less sulphuric acid. A marked difference occurs in the amount of chlorin present, there being over seven times as much chlorin, on an average, in the Tertiary shales as in the Cretaceous. This is the most conspicuous difference.

As an average, there occur to the acre 1,764 pounds of calcium bicarbonate, 23,320 pounds of calcium sulphate, 2,350 pounds of magnesium chlorid, 4,826 pounds of sodium chlorid, and 3,362 pounds of nitrate—that is, an average of 1.90 per cent of these shales is soluble in water and over 50 per cent of the salts consist of calcium sulphate or gypsum. The concentration of this material by underground-water movement, together with double decomposition, must result in enormous concentration of water-soluble salts.

The results of the analysis of the soluble-salt content of the ash is recorded in Table X. There is a marked increase in the sulphates and chlorids as compared with the composition of the shale. The calcium, magnesium, and carbonates decrease slightly. The increase is therefore due to the presence of salts of sodium.

TABLE X.—*Soluble salts in the Tertiary ash*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
41	Kings Meadow, Utah	26,704	1,494	920	4,181	217,640
42	.....do	7,538	1,346	640	2,774	136,840
222	Millburn, Wyo.	5,133	856	640	37,828	709
298	Myton, Utah	7,619	944	640	184,040	Trace.
40	Sigurd, Utah	2,566	843	580	1,679	4,572
217	Millburn, Wyo	7,456	962	840	156,000	1,417
309	Utahn, Utah	2,326	1,223	960	147,120	57
46	Richfield, Utah	1,844	716	320	4,782	284
218	Millburn, Wyo	7,218	1,136	800	178,720	227
38	Richfield, Utah	1,845	681	760	2,206	5,672
1	Nephi, Utah	602	None.	2,100	1,465	26,664
3	.....do	641	...do ..	1,220	6,103	993
8	.....do	1,443	...do ..	420	2,269	14,320
2	.....do	400	...do ..	640	255	None.

As an average, there are 1,107 pounds of calcium bicarbonate, 15,017 pounds of calcium sulphate, 3,665 pounds of magnesium sulphate, 59,595 pounds of sodium sulphate, 11,315 pounds of sodium chlorid, and 4,715 pounds of sodium nitrate—that is, 4.77 per cent of the ashy material are soluble in water. The predominating salt is sodium sulphate, over 30 per cent consisting of this material. The salt next present in greatest quantity is calcium sulphate closely followed by sodium chlorid. As an average, the amount of nitric nitrogen in the shale is 280 parts per million, while the amount of chlorin is 4,603, the ratio being 1 to 16.9. The ash which is the result of concentration of salts on the surface of the shale contains 390 parts per million of nitric nitrogen and 6,597 parts per million of chlorin, the ratio of which is likewise 1 to 16.9.

The soluble salts present in the virgin alkali collected in the undisturbed condition in the hills consists largely of the chlorid and sulphate of sodium, with appreciable quantities of calcium and magnesium sul-

phate. The results obtained on analysis are recorded in Table XI as pounds per 2,000,000 of material. The alkali salts near Myton (sample 301) consist in places largely of the sulphate of sodium. This contains 943 pounds of calcium bicarbonate, 26,435 pounds of calcium sulphate, 3,495 pounds of magnesium sulphate, 847,482 pounds of sodium sulphate, 2,890 pounds of sodium chlorid, and 113 pounds of sodium nitrate—that is, a total of 44 per cent of this alkali material is soluble in water, and the soluble material is 96 per cent pure sodium sulphate. There are nearly 2 per cent of calcium sulphate, with small amounts of magnesium sulphate, sodium chlorid, and sodium nitrate.

TABLE XI.—*Soluble salts in alkali of Tertiary origin*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
303	Myton, Utah	8,692	874	933	227,800	899
221	Millburn, Wyo.	28,232	7,129	27,200	274,400	12,760
298	Myton, Utah	7,699	943	640	184,040	Trace.
234	Lyman, Wyo.	6,015	297	1,080	125,600	1,843
204	Millburn, Wyo.	24,060	3,705	2,160	74,996	3,120
243	Superior, Wyo.	5,372	42,304	920	16,832	2,556
311	Utahn, Utah.	1,203	1,170	14,600	261,360	993
53	Grass Valley, Utah.	25,344	27,592	2,000	275,940	25,096
47	Glenwood, Utah.	4,332	367	480	8,724	330,720
237	Lyman, Wyo.	6,176	769	800	242,360	4,112
301	Myton, Utah	8,019	699	1,840	586,400	170
302	do	6,576	436	560	180,320	85
52	Greenwich, Utah.	19,488	4,158	800	117,760	19,000
230	Lyman, Wyo.	7,136	822	1,080	77,296	3,630
206	Millburn, Wyo.	19,728	11,978	3,480	258,040	13,328
51	Greenwich, Utah.	1,604	506	680	10,024	425
11	Nephi, Utah.	481	None.	3,320	3,058	12,478
227	Lyman, Wyo.	7,779	1,957	2,440	303,760	24,712
Average.	Tertiary.	10,180	7,479	2,815	187,618	24,718

As an average of all the samples collected, the proportion is not so extreme as this. There are 3,800 pounds of calcium bicarbonate, 31,280 pounds of calcium sulphate, 37,380 pounds of magnesium sulphate, 194,400 pounds of sodium sulphate, 142,020 pounds of sodium chlorid, and 420 pounds of sodium nitrate.

The soluble-salt content of the clay is recorded in Table XII. There is a marked individual variation in the results from the clay. Samples 4, 5, and 12 represent the clay lying immediately above the important salt deposits at Nephi and are really good samples of impure rock salt. Averages of the Tertiary clay, which includes these samples, therefore mean very little. In some individual samples the magnesium salts are entirely absent. Carbonates and sulphates of calcium are always present. With the exception of two cases, chlorin is always present.

TABLE XII.—*Soluble salts in clay and soil in place of Tertiary origin*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of samples.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
12	Nephi, Utah	7,540	None.	300	35,440	1,172 000
4	do	11,028	None.	280	23,872	925,900
231	Lyman, Wyo.	10,272	1,757	1,400	135,240	13,048
14	Nephi, Utah	24,700	None.	480	61,760	567
216	Millburn, Wyo.	401	367	1,600	9,296	Trace.
235	Lyman, Wyo.	2,724	926	1,000	25,760	425
19	Fountain Green, Utah	600	None.	600	3,654	None.
20	Richfield, Utah	11,388	825	280	33,392	1,205
228	Lyman, Wyo.	3,047	1,607	960	110,400	142
17	Nephi, Utah	842	None.	620	971	1,630
13	do	1,604	None.	720	1,201	10,998
7	do	802	None.	1,160	2,057	17,725
6	do	3,088	1,153	400	608	22,476
207	Millburn, Wyo.	5,856	1,573	720	19,918	992
5	Nephi, Utah	5,614	None.	400	1,448	104,280
54	Grass Valley, Utah	10,708	930	260	29,880	None.
Average.	Tertiary	6,263	571	699	30,880	141,961

The results for the analysis of the sandstone, shale, alkali, and ash of the Jurassic are all recorded in Table XIII. One very significant fact is the low results for water-soluble salts in the sandstone and shale. Another is the fact that only the carbonates, chlorids, sulphates, and nitrates of calcium and magnesium are present. Salts of sodium are absent or present only in very small quantities.

Thus, in the sandstone there are, as an average, 874 pounds of calcium bicarbonate; 5,634 pounds of calcium sulphate, 1,156 pounds of calcium chlorid, 2,600 pounds of magnesium chlorid, and 1,980 pounds of sodium nitrate per 2,000,000 pounds of material. There is 0.607 per cent of soluble material, nearly 50 per cent of which is calcium sulphate.

Likewise, in the shales the salts consist largely of the carbonates, sulphates, and chlorids of calcium and magnesium. There is 500 pounds of calcium bicarbonate, 3,182 pounds of calcium sulphate, 2,430 pounds of magnesium sulphate, 855 pounds of magnesium chlorid, and 98 pounds of sodium nitrate. There is 0.30 per cent of soluble salts in the shales, over 50 per cent of these salts being calcium sulphate.

The alkali material is not widely prevalent in the cultivated soil derived from the Jurassic either in the native virgin or cultivated soils The alkali here reported consists of the leaching from beneath the sandstone. Occasionally the underpart of the sandstone decays very rapidly, and white incrustations are deposited immediately beneath the rotten sandstone. One sample, No. 259, of this material was collected. Another sample, No. 288, consisting of crystalline material, was also collected. The alkali accumulations, or niter spots, prevalent in the soils derived from other geologic formations, were not observed by us in the Jurassic. Three samples of the ashy material were collected from beneath the

rotten sandstone or immediately above the gypsum deposits. Both the alkali and ash materials consist largely of the sulphates of calcium, magnesium, and sodium, with small amounts of calcium bicarbonate, sodium chlorid, and sodium nitrate.

TABLE XIII.—*Soluble salts in Jurassic material*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of samples.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
SANDSTONE						
283	Vernal, Utah	3,048	1,485	1,040	809	2,836
25	Richfield, Utah	3,248	None.	360	8,402	15,668
250	Moab, Utah	3,929	611	440	10,108	None.
254	do	962	672	816	329	284
255	do	1,443	515	640	2,107	425
251	do	1,684	699	480	2,535	284
253	do	1,524	637	760	3,885	Trace.
Average	Jurassic	2,263	660	648	4,025	2,785
SHALES						
284	Vernal, Utah	834	262	776	4,246	Trace.
24	Richfield, Utah	5,213	7,224	1,040	31,176	3,048
285	Vernal, Utah	1,925	236	1,132	1,546	284
23	Richfield, Utah	1,165	2,053	380	1,893	2,978
10	Nephi, Utah	1,524	None.	380	3,045	71
Average	Jurassic	1,066	997	370	4,190	638
ALKALI						
259	Moab, Utah	1,283	786	840	12,412	3,686
288	Vernal, Utah	15,558	2,726	1,120	404,480	Trace.
Average	Utah	8,421	1,756	980	208,446	1,843
ASH						
252	Moab, Utah	7,940	26,072	960	217,960	4,960
293	Vernal, Utah	2,887	3,949	320	54,456	283
135	Emery, Utah	401	384	920	14,152	567
Average	Jurassic	3,742	10,135	733	85,522	1,937

Probably the most significant fact is the extremely small quantity of alkali salts present in the country rock of the Quaternary period collected from the Cache Valley, Utah. The soils of this area are very productive and for the most part are largely free from alkali, especially as compared with the soils of the other areas studied. Large alkali areas such as occur elsewhere in the far West are unknown in this section. Nineteen representative samples of the country rock from this district were collected. The amount of soluble salts were so small that it was not thought worth while to make an analysis for the individual salts

and only the results for total salts are therefore available. These results are recorded in Table XIV. The amount of material is very small and as an average is 0.24 per cent.

TABLE XIV.—*Soluble salts in Quaternary material from Cache Valley, Utah*

[Results expressed as pounds per 2,000,000 of material]

Sample No.	158	167	165	164	166	161	149	136	160
Total salts	3,360	880	3,600	7,200	3,920	3,440	11,360	4,560	4,160

Sample No.	162	172	176	175	153	154	155	150	162	168
Total salts	2,240	6,800	3,360	6,400	2,160	8,800	16,880	3,600	3,280	2,080

Average 4,904 pounds, or 0.24 per cent of total salts.

Considerable concentration must take place over large areas to cause the production of alkali soils such as occur elsewhere. It is not surprising that there is not more alkali in the Cache Valley.

SOLUBLE SALTS IN THE GYPSUM DEPOSITS

The State of Utah contains enormous deposits of gypsum. These deposits are not peculiar to any single geological area or locality. They are widely distributed throughout the State. Fourteen samples of this gypsum were collected and analyzed. The results are recorded in Table XV. As would be expected, the soluble material consists largely of the sulphates of calcium. As an average, 2.72 per cent are soluble in water, consisting almost entirely of calcium sulphate, 96 per cent of the total soluble being gypsum. As an average, there are 892 pounds of calcium bicarbonate, 52,500 pounds of calcium sulphate, and 1,152 pounds of magnesium chlorid.

TABLE XV—*Soluble salts in the gypsum deposits*

[Results expressed as pounds per 2,000,000 of material]

Field No.	Location of samples.	Geologic formation.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
247	Moab, Utah	Jurassic	22,856	11,096	1,440	9,536	8,080
34	Sigurd, Utah	Tertiary	24,384	576	320	71,360	284
257	Moab, Utah	Jurassic	4,009	262	640	18,764	284
249	do	do	13,552	1,031	1,280	31,408	Trace.
142	Emery, Utah	Cretaceous	320	582	1,840	19,750	284
246	Moab, Utah	Jurassic	23,096	943	1,000	55,248	425
138	Emery, Utah	Cretaceous	22,376	681	160	56,464	Trace.
258	Moab, Utah	Jurassic	1,004	489	680	5,300	None.
139	Emery, Utah	Cretaceous	22,376	751	200	57,216	284
21	Richfield, Utah	Tertiary	11,268	None.	280	31,672	283
35	Sigurd, Utah	do	24,384	192	440	61,552	Trace.
37	do	do	11,628	319	180	25,876	Do.
16	Nephi, Utah	do	12,188	None.	360	27,840	355
15	do	do	24,944	do	4,400	59,920	1,702
	Average		15,670	1,209	661	36,723	856

TABLE XVI—*Soluble salts in miscellaneous soil-forming material*

[Results expressed as pounds per 2,000,000 of material.]

Field No.	Location of sample.	Calcium (Ca).	Magnesium (Mg).	Carbonic acid (CO_3).	Sulphuric acid (SO_4).	Chlorin (Cl).
58	Greenwich, Utah	8,420	None.	640	21,724	851
226	Lyman, Wyo	None.	908	2,000	4,806	6,019
240	Superior, Wyo	962	978	880	1,119	567
219	Lyman, Wyo	1,925	2,237	2,160	2,160	851
267	Dragon, Colo	561	716	1,200	691	None.
239	Superior, Wyo	962	1,160	1,200	1,086	354
209	Lyman, Wyo	1,090	734	840	2,996	284
27	Nephi, Utah	1,042	1,484	600	8,104	7,232
58	Greenwich, Utah	8,420	None.	640	21,724	851
226	Lyman, Wyo	None.	908	2,000	4,806	6,019
240	Superior, Wyo	962	978	880	1,119	567
219	Lyman, Wyo	1,925	2,237	2,160	2,160	851
267	Dragon, Colo	561	716	1,200	691	None.
239	Superior, Wyo	962	1,160	1,200	1,086	354
209	Lyman, Wyo	1,090	734	840	2,996	284
27	Nephi, Utah	1,042	1,484	600	8,104	7,232
28	Richfield, Utah	2,406	2,140	2,000	40,480	4,688
29	do	2,005	2,796	2,200	29,722	2,836
220	Lyman, Wyo	1,283	891	1,000	6,056	284
26	Richfield, Utah	240	262	680	3,605	5,530
49	Greenwich, Utah	1,283	559	480	1,251	709
50	do	1,043	288	380	2,271	425
18	FountainGreen, Utah	441	None.	310	567	1,205
45	Greenwood, Utah	4,772	2,324	360	30,480	1,772
266	Dragon, Utah	641	699	1,200	691	None.
Average		1,710	1,099	1,068	9,223	1,977

In Table XVI are recorded the results of some analyses of material which do not readily fit into the classification previously recorded. Some of these samples contain appreciable quantities of soluble salts, while others do not contain material quantities. Thus, No. 267 and 266, representatives of the limestone deposits above the Cretaceous sandstone, contain only nominal amounts of soluble salts and are comparable with the country of the Quaternary deposits of Cache Valley. Other samples, such as No. 45 and 28, which possibly ought to be classified with the Tertiary material, contain appreciable quantities of alkali salts.

As an average of all determinations, this material contains 1,444 pounds of calcium bicarbonate, 4,535 pounds of calcium sulphate, 5,495 pounds of magnesium sulphate, 2,438 pounds of sodium sulphate, and 3,360 pounds of sodium chlorid—that is, 0.86 per cent of the material is soluble in water.

SUMMARY OF RESULTS

The results of these investigations show a marked amount of water-soluble salts or alkali in the undistributed country rock with local accumulation wherever the movement of the underground water has

caused a local concentration by seepage through the rock and deposition by evaporation. There is a marked variation in the amount of salts occurring in the country rock in any given geological series. But uniformly high results have been obtained at widely separated sections of the country, such as those found at Grand Junction, Colo., Emery and Vernal, Utah, and Lyman, Wyo. There is a marked concentration of nitrates and alkali in the ashlike and alkali deposits in the uncultivated areas.

The following summary (Table XVII) shows the average alkali material found in the country rock.

TABLE XVII.—*Average alkali material in country rock*

CRETACEOUS MATERIAL

[Results expressed as pounds per 2,000,000]

Material.	Calcium.		Magnesium.			Sodium.			Total.
	Bicarbonate.	Sulphate.	Sulphate.	Chlorid.	Nitrate.	Sulphate.	Chlorid.	Nitrate.	
									Per cent.
Sandstone	983	16,469	3,922	985	1,961	.....	.....	.....	1.21
Shale	993	15,738	10,780	.....	.....	13,036	1,148	2,079	2.19
Clay	1,021	18,091	7,780	.....	.....	9,411	1,999	775	1.75
Ash	1,073	21,743	14,035	.....	.....	99,910	2,380	3,623	7.13
Alkali	3,419	35,666	127,235	.....	.....	152,682	17,665	5,492	17.1

TERTIARY MATERIAL

Sandstone	1,904	2,621	1,175	1,416	2,536	.....	.....	.....	.45
Shale	1,764	23,320	2,350	2,352	.....	.....	4,826	3,362	1.90
Ash	1,107	25,017	3,665	.....	.....	59,595	11,315	4,715	4.77
Alkali	3,800	31,280	37,380	.....	.....	194,400	142,020	420	20.46

JURASSIC MATERIAL

Sandstone[a]	874	5,634	.....	2,600	.....	.....	.....	1,980	.60
Shale	500	3,182	2,430	855	.....	.....	.....	98	.30

[a] Also 1,156 pounds of calcium chlorid present.

The summary brings clearly to mind the fact that in a widely disseminated form there is in the shales and sandstones of the Cretaceous and Tertiary of Utah, Colorado, and Wyoming enormous deposits of soluble salts consisting of the sulphates, chlorids, nitrates, and bicarbonates of calcium, magnesium, and sodium. In certain local areas these salts become concentrated so as to produce native alkali, or "niter spots," by the movement of the underground water without the instrumentality of the irrigation ditch. Wherever the shale is highly impregnated with the salts the evaporation of the water deposits the alkali salts on the surface in the form of an ashlike powder.

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EFFECT OF PARAFFIN ON THE ACCUMULATION OF AMMONIA AND NITRATES IN THE SOIL

By P. L. GAINEY,
Soil Bacteriologist, Kansas Agricultural Experiment Station

INTRODUCTION

For many years paraffin has found a wide use in the study of soil biology, plant physiology, soil fertility, mycology, and kindred subjects. Its peculiar physical properties, chemical inactivity, and comparative resistance to biological activity render it especially adapted to a variety of uses in these sciences. In many instances it is capable of rendering very valuable service. It is the purpose of this preliminary report, however, to call attention to certain dangers attendant upon such widespread use.

Perhaps the widest use of paraffin in the studies previously mentioned has been in the "paraffin wire-basket method" of studying soil fertility, a method recommended by the Bureau of Soils, United States Department of Agriculture (1) [1] and in a large number of variations from this method where paraffin is used to accomplish the same end. The object of its use in such instances has been in most cases to surround the medium (soil or solution) with a substance of a very inactive nature, impervious to both water and air. The principle of the above method as recommended by the Bureau of Soils and later adapted to physiological as well as fertility studies, consisted in substituting wire baskets coated with paraffin for the metallic or earthenware containers more commonly employed for such purposes.

According to Whitney and Cameron (9, p. 38),

> this form of basket has been eminently satisfactory.

Hoffmann (5) also has recommended the use of a paraffin block as a means of supporting seedlings growing in cultural solutions. Various modifications of this method have found use in a number of laboratories.

The Michigan Experiment Station (2) has made rather extensive use of paraffin oil in the separation of a soil solution to be used subsequently in chemical and physiological investigations of soil-fertility problems. Other instances are recorded in which the use of paraffin has been recommended in biological and cultural studies.

EXPERIMENTAL WORK

In experimental work to ascertain whether aeration can take place sufficiently in an uncultivated soil to maintain aerobic conditions in the subsurface, it became necessary to use a substance of a physical nature similar to paraffin. The commercial Parowax, prepared for the trade by

[1] Reference is made by number to "Literature cited," pp. 363-364.

the Standard Oil Co., was found to be admirably suited physically for this purpose. The method of study consisted in transferring to glass jars solid undisturbed cores of soil 5 inches in diameter and of varying length and in preventing aeration except through the normal surface. Subsequent measurements of the nitrate-nitrogen content at varying depths were made. To prevent aeration on the sides and bottom, melted Parowax was poured around the column of soil until it filled the space between the soil and jar, thus very effectually preventing the access of oxygen except from surface. A large number of experiments of this nature, in which aeration was varied by drawing a current of air through the column and by varying the physical condition of the column of soil, were carefully planned and executed.

In all instances where the Parowax came in intimate contact with the soil the accumulation of nitrate nitrogen, in spite of the fact that the other conditions favored nitrification, was so irregular and so unexpected that the results were absolutely inexplicable. The only outstanding fact to be gathered from the mass of data accumulated from the experiments was the apparent inhibitory effect the Parowax exerted upon the accumulation of nitrate nitrogen.

It was thought possible that the Parowax contained something toxic to the nitrifying organisms, but the substitution of paraffin prepared by Sargent & Co. for scientific purposes (M. P. 50°) did not alter the results. Studies were therefore initiated to ascertain, qualitatively and quantitatively, just what effect such substances produced upon biological activity in general and particularly upon the accumulation of nitrate nitrogen in the soil. In Tables I, II, and III are given data secured from typical experiments.

In all these experiments a soil possessing a vigorous ammonia and nitrate-forming flora was used in 100-gm. samples. From the results of the controls, in which no paraffin was used, the activity of the flora is shown to be very vigorous. The containers in all experiments were 500-c. c. wide-mouthed cotton-plugged bottles. Calcium carbonate was added to some samples and not to others. Samples were incubated with no addition of nitrogen, with nitrogen in the form of ammonium sulphate, and with nitrogen in the form of cottonseed meal. Incubation was in all cases at room temperature, and the moisture loss was replaced at frequent intervals. Where bottles are spoken of as being "Parowaxed" or "paraffined" the hot, melted substance was poured into the bottle, which was tilted so that the liquid would come in contact with all the inner surface, and the excess poured off. Where paraffin and Parowax were added direct to the soil, they were in the form of thin shavings made by scraping a cold bar of the solid substance. Paraffin oil was added by measuring from a pipette the desired quantity. After all additions were made and thoroughly mixed in, the moisture content of the soil was adjusted to optimum.

Nitrate nitrogen was determined colorimetrically and is reported as milligrams of NO_3 per 100 gm. of soil. Ammonia nitrogen was determined by the magnesium-oxid distillation method and reported as

milligrams of nitrogen per 100 gm. of soil. "Active nitrogen" represents the total quantity of nitrogen present both as NO_3 and NH_3. Ammonia was tested qualitatively with Nessler's reagent. Where it is reported as a "trace," only slight color resulted from the test. Where it is reported as "good," a strong yellow color was developed. Where it is reported as "abundant," a heavy brick-red precipitate was formed when the reagent was added to the clear solution.

RESULTS OF EXPERIMENTATION

The results presented in Tables I, II, and III are certainly very striking and show conclusively that paraffin can not be employed in investigations such as are mentioned earlier in this paper, unless the microbial flora is absolutely under control as regards the species present in the biological pabulum.

When nitrogen was not added, regardless of whether calcium carbonate was added, the presence of paraffin in the three forms here used completely inhibited the accumulation of both ammonia and nitrate nitrogen. Not only did it prevent further accumulations of nitrate nitrogen but actually caused all that was present at the beginning of the experiments to disappear. The effect was maintained for the longest period here recorded, 13 weeks, and similar results have been observed for even longer periods of incubation. The above relations held true whether the paraffin was intimately mixed into the soil or simply lined the inner wall of the container. In the latter case the quantity of paraffin actually coming in contact with the soil was rather limited.

When cottonseed meal was added as a source of nitrogen, vigorous ammonia and nitrate formation took place in the presence of paraffin. Owing to the very rapid subsequent disappearance of both ammonia and nitrate nitrogen, their formation is sometimes not apparent, and it is impossible to say whether such formation was equally as rapid as in the absence of paraffin. In no case after the 2-week analysis does the quantity of ammonia or nitrate nitrogen, where Parowax or paraffin was present, even approach the quantity in the controls. Differences in favor of the controls are evident even at the end of one week, and with both these forms of paraffin the active nitrogen (NO_3+NH_3) soon falls to a mere trace. Where paraffin oil was added, the results are somewhat different. During the early stages of incubation the inhibitory effect upon the accumulation of both forms of nitrogen is more marked than with other forms of paraffin. In the case of the oil the effect appears to be quite largely an inhibition of formation rather than a disappearance of ammonia and nitrate nitrogen, for, as incubation progresses, the quantity of active nitrogen approaches very closely that present in the controls. The decreased accumulation of both forms of nitrogen in the presence of Parowax and paraffin is more marked where they are mixed into the soil than where only surrounding it.

TABLE I.—*Effect of paraffin and Parowax upon the accumulation of nitrate and ammonia nitrogen in soil; with calcium carbonate*

[Results expressed as milligrams of NO_3 or milligrams of nitrogen as NH_3 per 100-gm. of soil]

No.	Treatment.	Quantity of nitrogen added.	2 weeks' incubation.		4 weeks' incubation.		12 weeks' incubation.	
			NO_3.	NH_3.[a]	NO_3.	NH_3.[a]	NO_3.	NH_3.[a]
1	None	None	5.3	Good reaction.	5.0	Good reaction.	7.0	Good reaction.
2	Calcium carbonate, 0.5 gm.	do	5.8	do	6.1	do	20.4	Trace.
3	Bottle paraffined	do	T.[b]	Trace	T.	Trace	T.	Do.
4	Calcium carbonate, 0.5 gm.; bottle paraffined	do	T.	do	T.	do	T.	Do.
5	Bottle Parowaxed	do	T.	do	T.	do	T.	Do.
6	Calcium carbonate, 0.5 gm.; bottle Parowaxed	do	T.	do	T.	do	T.	Do.
7	Paraffin, 2 gm.	do	T.	do	T.	do	T.	Do.
8	Calcium carbonate, 0.5 gm.; paraffin, 2 gm.	do	T.	do	T.	do	T.	Do.
9	Parowax, 2 gm.	do	T.	do	T.	do	T.	Do.
10	Calcium carbonate, 0.5 gm.; Parowax, 2 gm.	do	T.	do	T.	do	T.	Do.
11	Calcium carbonate, 0.5 gm.	30 mgm. as ammonium sulphate	5.7	Abundant	6.0	Abundant	100.0	Do.
12	Calcium carbonate, 0.5 gm.; bottle paraffined	do	5.3	do	4.1	do	41.0	Do.
13	Calcium carbonate, 0.5 gm.; bottle Parowaxed	do	5.1	do	2.2	do	45.0	Good reaction.
14	Calcium carbonate, 0.5 gm.; paraffin, 2 gm.	do	5.0	do	5.0	do	28.1	Trace.
15	Calcium carbonate, 0.5 gm.; Parowax, 2 gm.	do	4.5	do	4.5	do	37.5	Do.
16	Calcium carbonate, 0.5 gm.	30 mgm. as cottonseed meal	1.9	do	2.2	do	112.5	Do.
17	Calcium carbonate, 0.5 gm.; bottle paraffined	do	.8	do	0.0	do	0.0	Good reaction.
18	Calcium carbonate, 0.5 gm.; bottle Parowaxed	do	.3	do	0.0	do	.....	.....
19	Calcium carbonate, 0.5 gm.; paraffin, 2 gm.	do	T.	do	0.0	Good reaction.	0.0	Trace.
20	Calcium carbonate, 0.5 gm.; Parowax, 2 gm.	do	1.2	do	0.0	do	0.0	Do.

[a] NH_3 tested qualitatively.

[b] T. = trace.

TABLE II.—*Effect of Parowax and paraffin upon the accumulation of nitrate and ammonia nitrogen in soil*

[Results expressed as milligrams of NO_3 or milligrams of nitrogen as NH_3 per 100 gm. of soil]

No.	Treatment.	Quantity of nitrogen added.	2 weeks' incubation.		5 weeks' incubation.		13 weeks' incubation.		NH_3 (quantitative).	Active nitrogen.[a]
			NO_3.	NH_3 (qualitative).	NO_3.	NH_3 (qualitative).	NO_3.	NH_3 (qualitative).		
1	None	None	3.7	Trace	6.0	Trace	6.4	Trace	1.23	2.67
2	Bottle Parowaxed	do	0.0	do	0.0	do	Tr.	do	[b] 1.23	1.23
3	Bottle paraffined	do	0.0	do	0.0	do	0.0	do	[b] 1.23	1.23
4	Parowax, 2 gm	do	0.0	do	0.0	do	0.0	do	[b] 1.23	1.23
5	Paraffin, 2 gm	do	0.0	do	0.0	do	0.0	do	[b] 1.23	1.23
6	None	30 mgm. as ammonium sulphate	12.8	Abundant	28.2	Abundant	45.0	Abundant	14.43	24.55
7	Bottle Parowaxed	do	11.4	do	22.5	do	28.2	do	9.48	15.82
8	Bottle paraffined	do	11.4	do	26.4	do	32.1	do	9.00	16.22
9	Parowax, 2 gm	do	11.4	do	15.8	do	25.0	do	9.08	14.70
10	Paraffin, 2 gm	do	9.0	do	12.8	do	13.5	do	4.11	7.15
11	None	30 mgm. as cottonseed meal	22.5	do	75.0	Good reaction	53.1	do	4.53	16.48
12	Bottle Parowaxed	do	15.0	do	22.5	Trace	18.0	Trace	1.65	5.70
13	Bottle paraffined	do	18.0	do	56.2	Good reaction	22.5	do	[b] 1.65	6.71
14	Parowax, 2 gm	do	9.6	Good reaction	Tr.	Trace	Tr.	do	[b] 1.65	1.65
15	Paraffin, 2 gm	do	7.7	do	0.0	do	0.0	do	[b] 1.65	1.65

[a] Active nitrogen is NO_3 nitrogen + NH_3 nitrogen.

[b] Figures estimated from other analyses showing similar qualitative results.

TABLE III.—*Effect of paraffin, Parowax, and paraffin oil upon the accumulation of nitrate and ammonia nitrogen in soil*

[Results expressed as milligrams of NO_3 or miligrams of nitrogen as NH_3 per 100 gm. of soil]

No.	Treatment.	Quantity of nitrogen added.	1 week incubation.				2 weeks' incubation.			
			NO_3	NH_3		Active nitrogen.	NO_3	NH_3		Active nitrogen.
				Qualitative.	Quantitative.			Qualitative.	Quantitative.	
1	None	None	2.8	Trace			4.6	Good reaction		
2	Paraffin, 2 gm	do	2.8	do			1.1	Trace		
3	Parowax, 2 gm	do	2.4				0.5	do		
4	Paraffin oil, 2 gm	do	1.2	Trace			Trace.	do		
5	None	50 mgm. as ammonium sulphate	4.6	Abundant			13.1	Abundant		
6	Paraffin, 2 gm	do	4.6	do			14.1	do		
7	Parowax, 2 gm	do	4.8	do			15.2	do		
8	Paraffin oil, 2 gm	do	3.8	do			12.0	do		
9	None	50 mgm. as cottonseed meal	4.1	do	23.83	24.75	15.0	do	26.77	30.15
10	Paraffin, 2 gm	do	3.5	do	18.11	18.90	13.3	do	16.07	19.06
11	Parowax, 2 gm	do	3.5	do	20.39	21.17	14.1	do	24.64	27.81
12	Paraffin oil, 2 gm	do	2.4	do	15.25	15.79	10.0	do	23.03	25.28

No.	Treatment.	Quantity of nitrogen added.	4 weeks' incubation.				6 weeks' incubation.				8 weeks' incubation.			
			NO_3	NH_3		Active nitrogen.	NO_3	NH_3		Active nitrogen.	NO_3	NH_3		Active nitrogen.
				Qualitative.	Quantitative.			Qualitative.	Quantitative.			Qualitative.	Quantitative.	
1	None	None	6.7	Trace			5.5	Trace	1.16	2.40	10.2	Trace		2.3
2	Paraffin, 2 gm	do	1.8	do			Trace.	do	1.16	1.16	Trace.	do		
3	Parowax, 2 gm	do	1.8	do			Trace.	do	1.16	1.16	Trace.	do		
4	Paraffin oil, 2 gm	do	2.0	do			Trace.	do	[a]1.16	1.16	Trace.	do		
5	None	50 mgm. as ammonium sulphate.	90.0	Abundant			120.0	Good reaction	2.80	29.80	180.0	do		40.5
6	Paraffin, 2 gm	do	48.6	do			60.0	Abundant	6.60	20.10	105.0	do		23.6
7	Parowax, 2 gm	do	52.8	do			72.0	do	4.46	20.66	121.0	do		27.2
8	Paraffin oil, 2 gm	do	50.7	do			100.0	do	9.40	31.90	180.0	do		40.5
9	None	50 mgm. as cottonseed meal.	100.0	Good reaction.	6.10	28.60	90.0	Trace	[a]2.48	22.73	121.0	do		27.2
10	Paraffin, 2 gm	do	14.0	Trace	2.64	5.79	Trace.	do	[a]2.48	2.48	Trace.	do		
11	Parowax, 2 gm	do	40.5	do	2.06	11.17	Trace.	do	2.48	2.48	Trace.	do		
12	Paraffin oil, 2 gm	do	56.0	Abundant	15.00	27.60	69.0	do	[a]2.48	18.00	106.0	do		23.8

[a] Estimated.

When ammonium sulphate was added to the soil either with or without calcium carbonate, all three forms of paraffin exerted a very marked effect upon the accumulation of nitrate nitrogen. The decreased accumulation of nitrate nitrogen was not so evident during the early stages of incubation except with paraffin oil. With the oil the effect again seems to be to retard nitrification, the quantity of active nitrogen approaching very closely that in the controls. Parowax and paraffin, however, not only decrease the accumulation of nitrate nitrogen but also bring about a large reduction in the quantity of active nitrogen. The reduction in active nitrogen occasioned by the various forms of paraffin is not nearly so rapid where ammonium sulphate was added as where nitrogen in the form of cottonseed meal was added. This is probably due to the food elements other than nitrogen contained in the cottonseed meal.

In the experiments thus far given the mass of soil used was only 100 gm. In order to ascertain whether coating the containing vessel with paraffin would exercise an appreciable effect upon NO_3 accumulation if the volume of soil were larger, the following experiments were carried out. The inside of a glass jar 5 inches in diameter was coated with paraffin, another was coated with Parowax, and a third was left untreated. The jars were all filled with loose soil containing optimum moisture and calcium carbonate. After seven weeks of incubation the soil of each jar was mixed and analyzed for NO_3. The following quantities, expressed as milligrams of NO_3 per 100 gm. of soil, were found to be present: Untreated jar, 7.1 mgm.; paraffined jar, trace; Parowaxed jar, trace.

At the same time a 2-gallon earthenware jar 8¼ inches in diameter coated on the inside with paraffin and another untreated were filled with the same soil and incubated the same length of time. Upon analysis a central column of soil 2¼ inches in diameter was removed from each jar and analyzed separately. The milligrams of NO_3 per 100 gm. of soil from the central core and from the remaining soil in each jar were as follows:

	Center.	Remainder.
Untreated jar	7.6	7.8
Paraffined jar	5.3	1.2

The closest that the central column came to the surrounding paraffin was 3 inches, yet the paraffin caused a reduction of approximately one-third in the accumulation of nitrate nitrogen. It is evident, therefore, that the effect of paraffin upon NO_3 accumulation can be exerted over an appreciable distance. These experiments show that no ordinary sized container used for cultural purposes can be protected with a coating of paraffin, as in these experiments, without the available nitrogen content throughout the whole mass of soil being affected.

DISCUSSION OF RESULTS

To what is this very marked effect of paraffin upon the accumulation of ammonia and nitrate nitrogen to be ascribed? Where the major differences are observed, the evidence does not seem to support the view that it is an inhibitory effect exerted upon the ammonifying and nitrifying organisms. There is evidence that such an effect may occur to a slight extent in some instances, but the very large actual disappearance of nitrate and ammonia nitrogen, one time present, certainly can not be ascribed to such a phenomenon. Since the experimental conditions were strictly aerobic, as the nitrification in controls and sometimes in treated samples will show, they would tend to eliminate denitrifying processes. The only other possibility lies in an actual metabolic consumption by organisms stimulated by the presence of paraffin. It is rather difficult to conceive of the consumption of such large quantities in this manner in such a short period of time, unless one has observed such cultures.

Parallel with the disappearance of active nitrogen, there has also been a disappearance of paraffin and an enormous development of certain species of fungi. This growth of saprophytic fungi was so abundant where ammonium sulphate and cottonseed meal were added that at the end of two to four weeks the cultures appeared to be almost solid masses of white hyphæ which later developed almost all varieties of color. In the absence of added nitrogen, while the growth was not sufficient to be macroscopically visible, other physical characteristics showed growth to be abundant.

Rahn (6) a number of years ago called attention to the presence in soil of a species of Penicillium capable of utilizing paraffin in its metabolism when grown in cultural solutions containing paraffin as the only organic constituent. Later Söhngen (7) isolated and studied from soils and other sources a number of species of bacteria capable of utilizing paraffin under similar conditions. It is not unreasonable, therefore, to assume that the enormous growth of fungi observed where paraffin was added utilized this as a source of carbon and energy; also that the active nitrogen observed to disappear was used as source of nitrogen in the metabolism of the fungi. Where no nitrogen was added, available nitrogen soon became the limiting factor in fungus growth. Growth under such conditions was accordingly much more limited. So long as nitrogen remained the limiting factor in growth, that present in a form capable of being utilized was consumed as rapidly as it became available. Ammonia and nitrate nitrogen are both readily available to many saprophytic bacteria and fungi; hence, the quantities of these two forms of nitrogen would be kept at a minimum. On the other hand, when ammonia or an organic substance capable of yielding ammonia in large

quantities was added, available nitrogen no longer became the limiting factor in fungus growth. Under such conditions the existence of ammonia or an accumulation of nitrate nitrogen to a limited extent became possible.

The extensive use of paraffin in the "paraffin wire-basket method" of studying soil fertility and in similar studies involving the same principles has been previously mentioned. It might be well to call attention to the extensive comparisons of the manurial requirements as ascertained by this method and in actual field tests conducted by the Rhode Island Station (3, 4, 8). This was probably the most comprehensive test of the reliability of the method ever carried out. As a summary of the results, Hartwell and Pember (4, p. 31) have the following to say:

> The frequent failure of the method to secure at different times similar indications regarding the deficiencies of a given soil, even when carried out in the same manner, is the most discouraging feature concerning the usefulness of the method. The many instances of disagreement between the results of the basket method and those secured in actual field practice render unreliable the indications which the method in its present form affords regarding the manurial requirements, at least of certain soils.

Hartwell and his associates offer no explanation of the anomalous results secured by this method, and, so far as we are aware, no one has explained why so many incorrect indications of manurial requirements were recorded. Wheeler, Brown, and Hogenson (8) do mention in one instance the possibility of denitrification where nitrate nitrogen was added in presence of manure, but attribute this possibility to the manure rather than to the method.

The results in the present paper undoubtedly offer a satisfactory explanation for the failure of the method we were using in the study of aeration in soils. In these results we also have a probable explanation of the failure of the "paraffin wire-basket method" in the hands of the Rhode Island investigators and in other instances where such failures may have been recorded. No doubt where such a stimulation of saprophytic development is brought about, not only will nitrogen but also other food elements required in growth be consumed. These facts must all be taken into consideration when paraffin is used in physiological or cultural experiments involving a mixed culture possibly containing organisms capable of utilizing paraffin in their metabolism. The value and significance of all results heretofore reported as secured under such conditions must also be discounted.

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VOLATILITY OF ORGANIC COMPOUNDS AS AN INDEX OF THE TOXICITY OF THEIR VAPORS TO INSECTS [1]

By WILLIAM MOORE, [2]
Head of Section of Research in Economic Zoology, Minnesota Agricultural Experiment Station

INTRODUCTION

In a previous paper [3] the writer pointed out the relationship between the toxicity of various benzene derivatives and their boiling points, citing the literature. The question arose whether a similar relationship of boiling point and toxicity existed among other volatile organic compounds. Early in the work it was discovered that boiling point was merely a convenient general index of the volatility of the compound and that the real relationship was probably between toxicity and volatility. It was at first thought that this relationship existed only with compounds having an action on lower organisms similar to that of chloroform and ether, but it was soon found to have a wider range of application.

METHOD OF EXPERIMENTATION

In general, the same methods were employed as in the previous work.[3] In order to hasten the rate of diffusion of the vapor throughout the flask, the piece of filter paper, with the chemical to be tested, was suspended in the center of the flask by means of a fine wire. The lead foil covering the stoppers was attacked by some of the acids used in the experiments, making it necessary in these cases to coat the stoppers with collodion. Many of the chemicals produced anesthesia, and, although the flies showed no signs of life, they recovered upon being removed from the flask. A new method was therefore employed in determining the amount of the chemical necessary to kill in 400 minutes. Flasks containing varying quantities of the chemical were started and all were stopped 400 minutes later. These exposed to the smaller doses usually revived; with slightly stronger doses only a partial revival was noticed; while the larger quantities of the chemical resulted in death. In this manner the actual amount necessary to kill in 400 minutes was determined.

In studying the volatility 0.5 c. c. of the liquid was spread over a ground-glass plate and the time necessary for this quantity to evaporate noted. Solids were powdered, and 1 gm. was spread out on the glass to

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evaporate. After a certain period, varying according to the volatility of the compound, the solid was weighed again, the loss in weight being the amount evaporated in that period of time. These data were then reduced to gram-molecules evaporated in 400 minutes.

The insect used in the tests was the housefly (*Musca domestica* L.), reared under natural conditions.

CHEMICALS TESTED

In the selection of the organic compounds to be tested the object was to obtain a series differing widely in their chemical composition and toxicology. Their possible use as insecticides was not considered, since the object of the investigation was to discover the general laws of toxicity of volatile organic compounds to insects.

The chemicals might be conveniently divided into hydrocarbons, esters, acids, ethers, hydrocarbon derivatives containing hydroxyls, aldehydes, ketones, halogens, sulphur or nitrogen, terpenes or terpene derivatives, and alkaloids. The following list is thus divided:

Hydrocarbons:
- Petroleum ether (pentane and hexane).
- Gasoline (mostly heptane).
- Kerosene (mostly nonane and decane).
- Benzene.
- Toluene.
- Xylene.
- Naphthalene.
- Camphene.

Acids:
- Acetic acid.
- Butyric acid.
- Valeric acid.

Aldehydes and ketones:
- Acetone.
- Acetaldehyde.
- Chloral hydrate.
- Brommethylphenylketone.
- Furfural.
- Menthone.

Sulphurs:
- Carbon bisulphid.
- Ethyl mercaptan.
- Allyl isosulphocyanate.
- Thiophene.

Terpenes and their derivatives:
- Camphene.
- Camphor.
- Menthone.
- Menthol.
- Pinene.
- Terpinol.
- Citral.

Terpenes and their derivatives—Contd.
- Eugenol.
- Isoeugenol.
- Geranyl acetate.

Esters:
- Methyl salicylate.
- Ethyl malonate.
- Ethyl acetoacetate.
- Amyl acetate.
- Amyl valerate.
- Propyl acetate.

Ethers:
- Ethyl ether.
- α-Naphthol ethyl ether.

Hydroxyls:
- Methyl alcohol.
- Ethyl alcohol.
- Amyl alcohol.
- Menthol.
- Thymol.

Halogens:
- Chloroform.
- Bromoform.
- Carbon tetrachlorid.
- Chloretone.
- Brometone.
- Ethylene bromid.

Nitrogen:
- Chlorpicrin.
- Amyl nitrite.
- Nitrobenzene.
- Pyridin.

Alkaloids:
- Nicotin.

EXPERIMENTAL RESULTS

Eugenol, isoeugenol, and α-napthol ethyl ether were so slightly volatile that more than 400 minutes were required for the death of the flies;

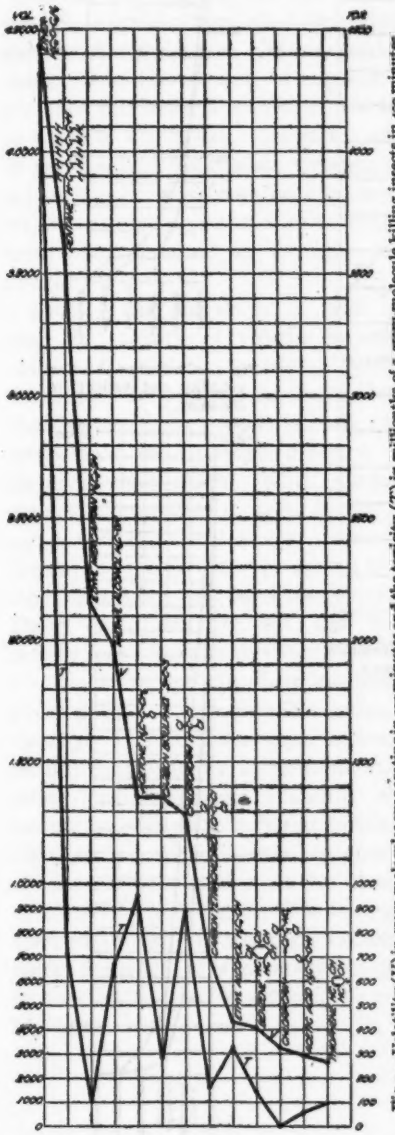

Fig. 1.—Volatility (*V*) in gram-molecules evaporating in 400 minutes and the toxicity (*T*) in millionths of a gram-molecule killing insects in 400 minutes.

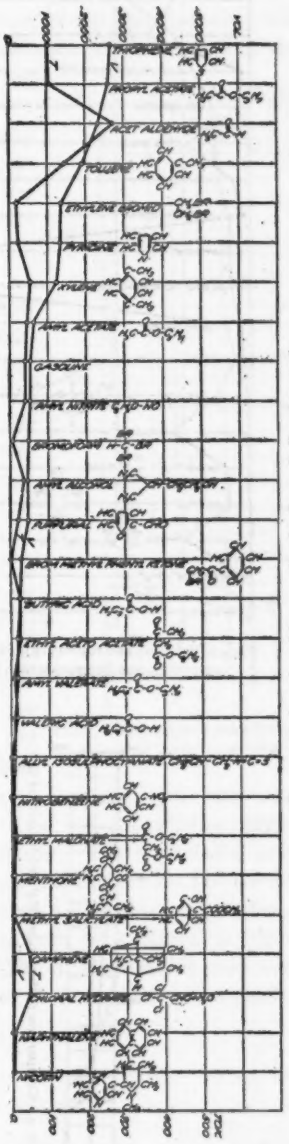

Fig. 2.—Continuation of figure 1, showing less volatile compounds.

hence, they are not included in the results. Pinene, terpinol geranyl acetate, and to some extent citral on exposure to the air, tend to form a

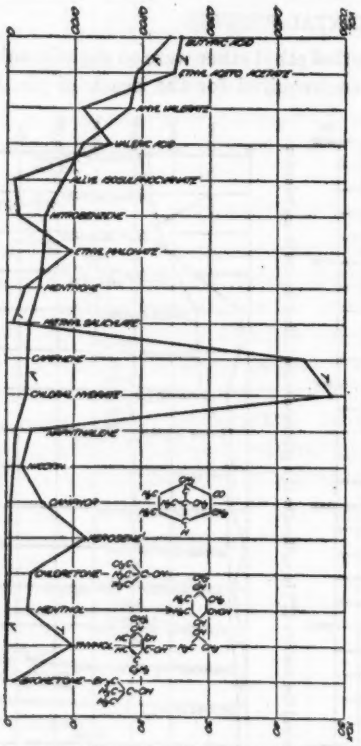

Fig. 3.—Volatility and toxicity of the slightly volatile compounds on a larger scale than in figure 2.

Fig. 4.—Comparison of the volatility and toxicity of the acids.

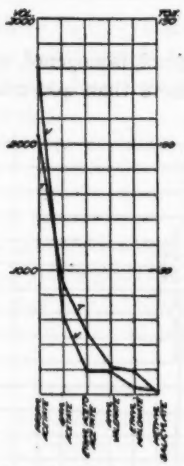

Fig. 5.—Comparison of the volatility and toxicity of the esters.

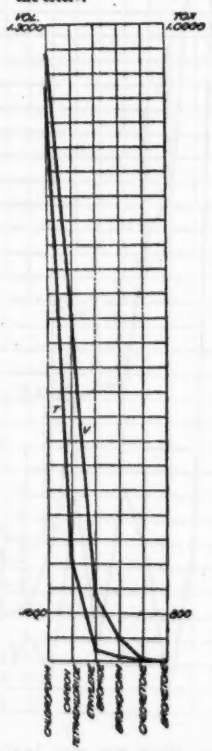

Fig. 6.—Comparison of the volatility and toxicity of the halogen derivatives.

gummy mass without completely evaporating. The toxicity of these compounds, particularly piene and terpinol, is variable. Pinene usually fails to kill the flies, while terpinol may kill with a certain dose one day, while the following day the same dose is not fatal. Usually unless the flies die in a short time after the introduction of the material, they will survive the fumigation. These erratic results are no doubt due to the oxidation of the terpene on exposure to the air, thus producing a substance which is not so toxic to the insect. Inasmuch as many of the essential oils contain terpenes producing such gummy residues on exposure to the air, it is at once apparent why varying results have been reported as to their value as insecticides.

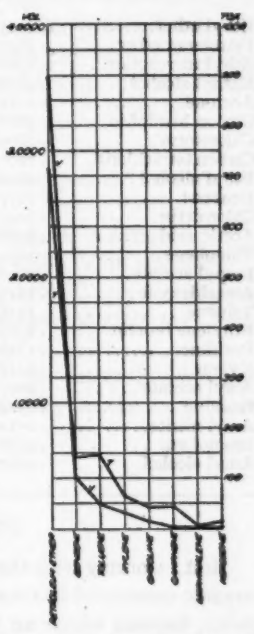

Fig. 7.—Comparison of volatility and toxicity of the hydrocarbons.

Table I and figures 1, 2, and 3 show that the toxicity of volatile organic compounds is closely correlated with their volatility. In general, the less volatile the chemical the more toxic it is even where the compounds are strikingly different in their chemical composition. When related compounds are considered, as in figures 4, 5, 6, and 7, this agreement is even more marked. Exceptions are noted, as in carbon bisulphid, ethyl mercaptan, and particularly chlorpicrin. These exceptions are not due to vapor density, nor primarily to water solubility, but are no doubt due to their chemical composition or to some peculiar action of the chemical. Hydrocyanic acid, although not included in this paper, would be an exception, owing to its extreme solubility in water and the fact that such minute quantities are sufficient to inhibit the action of oxidizing enzyms. Chlorpicrin may be likewise an enzym poison. The remarkable point of data here presented is not that there are a few exceptions, but the fact that there are so few exceptions among so large a number of very different chemicals which are strikingly different in their toxicological action on higher animals. It is interesting to note that ethyl alcohol is more toxic to insects than methyl alcohol, the reverse of that which takes place in higher animals

TABLE I.—*Relation of the volatility of organic compounds to their toxicity*

Name of compound.	Volatility in gram-molecules evaporating in 400 minutes.	Toxicity in millionths of a gram-molecule killing in 400 minutes.	Name of compound.	Volatility in gram-molecules evaporating in 400 minutes.	Toxicity in millionths of a gram-molecule killing in 400 minutes.
Ethyl ether	4.4245	4318.4	Furfural	.0457	20.8
Petroleum ether	3.5841	713.3	Brommethylphenyl-ketone	.0282	2.4
Ethyl mercaptan	2.1541	109.9	Butyric acid	.0241	25.8
Methyl alcohol	1.9776	671.8	Ethyl acetoacetate	.0192	24.8
Acetone	1.3631	954.3	Amyl valerate	.0182	11.2
Carbon bisulphid	1.3616	286.3	Valeric acid	.0113	15.3
Chloroform	1.2870	894.6	Allyl isosulphocyanate	.0085	1.2
Carbon tetrachlorid	.7067	161.9	Nitrobenzene	.0058	1.8
Ethyl alcohol	.4342	331.2	Ethyl malonate	.0054	9.6
Benzene	.4097	142.3	Menthone	.0049	2.9
Chlorpicrin	.3243	1.7	Methyl salicylate	.0033	1.0
Acetic acid	.2936	60.0	Camphene	.0032	44.0
Thiophene	.2659	102.2	Chloral hydrate	.0030	48.0
Propyl acetate	.2610	103.4	Naphthalene	.0013	3.9
Acetaldehyde	.2343	273.2	Nicotin	.0010	2.4
Toluene	.1918	147.5	Camphor	.00068	5.2
Ethylene bromid	.1363	18.6	Kerosene	.00067	11.9
Pyridine	.1347	21.7	Chloretone	.0005	3.6
Xylene	.1241	64.9	Menthol	.00019	3.2
Amyl acetate	.0627	44.8	Thymol	.00014	9.9
Gasoline	.0520	42.0	Brometone	.00009	1.1
Amyl nitrite	.0512	41.1			
Bromoform	.0486	7.7			
Amyl alcohol	.0460	38.2			

DISCUSSION OF RESULTS

Holt,[1] working with the cockroach, states that the toxicity of a volatile organic compound increases as the boiling point increases, up to a certain point, beyond which an increase in boiling point is accompanied by a decrease in toxicity. In the writer's own work the results show an increase in toxicity up to where the compound is so slightly volatile (b. p. 225° to 250° C.) as to be of no value. Holt used a fixed quantity of each compound in uniform flasks, giving the time required as an index of toxicity. Under such conditions a larger quantity of a high boiling point compound than would volatilize was placed in the flask. Although such compounds required longer to kill the cockroaches in Holt's flasks, the amount of vapor which produced the death was much less than was considered to be the case. The apparent decrease in toxicity in his experiments was really an increase, since the dose was greatly diminished, although the period of time was increased. The question naturally arises as to why the volatility of a chemical should be related to its toxicity. The following seems to be a reasonable explanation. The vapor present in the air is taken into the tracheæ of the insects and is

[1] HOLT, J. J. H. THE COCKROACH; ITS DESTRUCTION AND DISPERSAL. *In* Lancet, v. 190, no. 4840, p. 1136–1137. 1916.

condensed upon reaching their finer divisions. If the compound is very volatile, it will evaporate and readily pass out of the insect, while if very slightly volatile it will remain in the insect, and will penetrate the tissues and produce the poisonous reactions which lead to the insect's death. In higher animals, when the compound is taken into the lungs, it is rapidly removed by the blood and carried to all parts of the body, giving it an opportunity to react chemically with the tissues. For this reason the toxicity of volatile organic compounds is more closely correlated with the chemical composition when introduced into the higher animals, while in insects toxicity is more closely associated with volatility than with chemical composition.

SUMMARY

In general, the toxicity of a volatile organic compound is correlated closely with its volatility.

A decreasing volatility is accompanied by an increased toxicity.

The boiling point of the chemical is a general index of its volatility.

Compounds with boiling points of 225° to 250° C. are usually so slightly volatile that they do not produce death except after very long exposures.

The structure of the respiratory system of the insect is probably responsible for the remarkable influence of volatility on the toxicity of the vapor of volatile organic compounds.

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